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APPLIED CHEMISTRY;
IN MANUFACTURES, ETC.

VOL. II.

APPLIED CHEMISTRY;

IN

MANUFACTURES, ARTS, AND DOMESTIC ECONOMY.

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MANUFACTURE OF GLASS.

STARCH. TANNING.

CAOUTCHOUC; ITS PROPERTIES AND APPLICATIONS.

BORAX AND THE BORACIC LAGOONS.

SOAP.

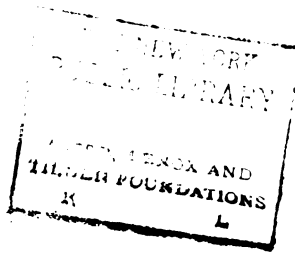
SULPHUR AND SULPHURIC ACID.

SODA MANUFACTURE.

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TABLE OF CONTENTS.

I. MANUFACTURE OF GLASS.

	PAGE
§ I. HISTORY OF THE GLASS MANUFACTURE	1
Pliny's account of the invention of glass.—Glass-works of Sidon, Alexandria, and Rome.—Portland or Barberini vase.—Glass-making introduced into Venice.—Progress of glass-making in France.	3
Invention of cast plate-glass.—St. Gobin glass-works.— <i>Glain neidyr</i> of the Druids.—Progress of glass-making in Britain.—British Plate-glass Company.	6
§ II. PROPERTIES OF GLASS, AND THE PRINCIPLES OF ITS MANUFACTURE	9
Physical properties of glass.—Properties of the constituents of glass.—Silicic acid.—Silicates of the alkalies.—Soluble glass.—Silicate of lime.—Silicate of alumina.—Silicates of lead.—Silicates of iron.—Silicates of manganese.	10
Chemical constitution of different kinds of glass	19
Properties of unannealed glass.—Annealing	20
Reaumur's porcelain	22
§ III. MATERIALS USED IN THE MANUFACTURE OF GLASS	24
Sand.—Flints.—Lime.—Soda-ash.—Soap-boilers' waste, alkaline sulphates, common salt, nitre.—Litharge, minium.—Cullet.—Black oxide of manganese.—Arsenious acid.	24
§ IV. DETAILS OF THE MANUFACTURE OF GLASS	33
Glass-houses.—Glass-pots	33
Flint-glass.—Flint-glass house and pots.—Materials for making flint-glass.—Glass-gall.—Modes of fashioning vessels of flint-glass.—Annealing.	35
Strass	44
Crown-glass.—Crown-glass house and pots.—Colear and other sub-	

	PAGE
sidialy furnaces.—Materials employed in making crown-glass.— Fritting.—Melting.—Flashing.—Annealing.	46
Bronz-glass	55
Bottle-glass	60
Plate-glass.—Materials for making plate-glass.—Ravenhead plate- glass works.—Founding.—Casting.—Annealing.—Grinding, smoothing, and polishing.—Silvering.—Blowing of plate-glass.	62
§ V. DEFECTS IN GLASS	75
Mixing, knots, threads and tears.—How to obtain uniform glass.— Flint-glass of M. Guinaud.—Experiments of Mr. Faraday on op- tical glass.	75
§ VI. COLOURING OF GLASS	80
Metallic oxides used for colouring glass.—Protoxide and suboxide of copper.—Peroxide and protoxide of iron.—Oxide of cobalt.— Oxide of chromium.—Oxide of manganese.—Oxide of gold.— Oxide of silver.—Oxide of uranium.—Chrome yellow.—Prot- oxide of platinum.	80
Materials employed to render glass translucent	87
Painting, printing, and staining of glass	88
Etching on glass	90
Glass grinding and cutting	93

II. STARCH.

§ I. PROPERTIES AND COMPOSITION OF STARCH	99
§ II. PREPARATION OF STARCH FROM THE CEREALS	109
Composition of wheat.—Preparation of starch from ground wheat by fermenting process.—"Boxing" and drying of starch.—Prepara- tion of starch from dough, by washing.—Preparation of starch from unground wheat.	109
§ III. PREPARATION OF STARCH FROM RICE	118
Composition of rice.—Separation of gluten from rice by an alkali ; —by an alkaline carbonate,—and by a dilute acid.	118
§ IV. PREPARATION OF STARCH FROM THE POTATOE	124
Composition of the potatoe.—Estimation of the proportion of starch in the potatoe.—Apparatus employed in the preparation of potatoe- starch.—Uses of potatoe-starch, and of the bye-products of the manufacture.	124

CONTENTS.

vii

PAGE

§. V. ARROW-ROOT ; SAGO ; TAPIOCA ; SALEP ; TOUS LES MOIS ; INDIAN-CORN STARCH	139
§ VI. DEXTRIN AND STARCH SUGAR	145
Action of dilute acids on starch.—Process of making starch-sugar. —Properties of starch-sugar.—Means of detecting adulteration of cane-sugar with starch-sugar.	145
Dextrin.—Modes of preparing dextrin.—Properties of dextrin.— Diastase.—Malting and brewing.	149
Use of starch as food	158

III. TANNING.

Principles of the process of tanning.—Composition and structure of the skin of animals.	161
§ I. PROPERTIES OF TANNIC ACID AND THE ASTRINGENT VEGETABLE MATTERS EMPLOYED IN TANNING	165
Different varieties of tannin.—Tannogelatin.—Preparation of tannin from gall-nuts.—Properties of tannin of gall-nuts.—Gallic acid.—Conversion of tannin into gallic acid.	165
Materials employed in tanning.—Oak-bark.—Sumach.—Divi-divi. —Valonia.—Catechu (terra).—Larch-bark.—Myrobalams.—Wil- low-bark.—Mimosa or wattle-bark.—Cork-tree-bark.	173
Relative value of different tanning materials	184
§ II. PREPARATION OF HIDES AND SKINS FOR TANNING	192
Relative value of different kinds of hides, kips, and skins	192
Preparation of hides	193
Treading.—Unhairing.—Liming.—Beaming.—Softening of roots of the hair by putrefactive processes, and by dilute acids.—Objections to the liming process.—New mode of unhairing and cleansing followed in America.	193
Preparation of kips and skins.—Grainer or bate.	204
§ III. MODES OF APPLYING TANNIN TO PREPARED HIDES AND SKINS	206
Old slow tanning process.—Common process followed at present.— Handlers and bloomers or layers.—Tanning by filtration.—Finishing operations.	206
Bloom.—Colour of leather.	214
Processes for expediting the tanning.—Processes of Mr. Spilsbury, Mr. Drake, Mr. Chaplin, and Messrs. Herepath and Cox.—Superior mechanical process.	220

	PAGE
Characters of good leather.—Leather made from split hides.—Cost of tanning.	227
Bordier's process for making leather from metallic preparations.—Mode of preserving hides intended to be tanned.	229
Currying	232
§ IV. PREPARATION OF LIGHT AND FANCY LEATHERS	234
Morocco leather	234
Skiver and roan	237
Leather prepared by means of alum (kid-leather)	237
Chamois leather	239
Russia leather	242

IV. CAOUTCHOUC; ITS PROPERTIES AND APPLICATIONS.

Sources and preparation of caoutchouc.—Properties of caoutchouc juice.—Properties of caoutchouc.—Composition of caoutchouc.	245
Solvents of caoutchouc.—Applications of the solutions of caoutchouc.—Mackintosh water-proof cloth.	251
Substitute for leather from caoutchouc	253
Use of caoutchouc in book-binding	254
Marine glue	254
Products of the distillation of caoutchouc.—Caoutchoucine.—Caoutchine.—Caoutchène.—Heveène.—Application of caoutchoucine.	254
Caoutchouc stoppers for bottles	256
Mode of combining shreds of caoutchouc into a lump, and then cutting into sheets.	257
Slabs for paving, roofing, &c. made of caoutchouc and sand or sawdust	258
History of the introduction of caoutchouc into Europe	259

V. BORAX AND THE BORACIC LAGOONS.

§ I. HISTORY AND PROPERTIES OF BORAX	261
Occurrence of borax in nature.—Tincal.	261
Process for refining tincal	262
Properties of borax	263
Applications of borax in soldering, glazing of earthenware, and glass-making	266
§ II. BORACIC ACID	267
Preparation of boracic acid from borax	267
Properties of boracic acid	268
Constitution of boracic acid.—Boron	269

CONTENTS.

ix

	PAGE
Occurrence of free boracic acid in nature.—Boracic lagoons of Tuscany.—Mode of separating the acid.	71
Views concerning the origin of the boracic acid and accompanying substances	279
§ III. MANUFACTURE OF BORAX FROM BORACIC ACID	282
Composition of crude boracic acid	282
Process of making borax with carbonate of soda and the native acid	283
Mode of making borax with nitrate of soda and the native acid	288
Mode of making borax in the dry way	289
Modes of detecting sophistication in borax	289
Neutral borate of soda	290

VI. SOAP.

§ I. GENERAL PRINCIPLES OF SOAP-MAKING PROCESSES	293
Chemical constitution of soaps and fixed oils.—Soluble and insoluble soaps ; plasters.—Hard and soft soaps.—Solubility of stearates and oleates of potash and soda.—Quantity of alkali required for saponification.—Soap of ammonia	293
§ II. MATERIALS EMPLOYED IN SOAP-MAKING	299
Alkaline leys	299
List of unctuous matters used in soap-making	301
Stearine.—Stearic acid.—Stearine candles.—Stearates of potash and soda. —Margarine. —Margaric acid. —Oleine.—Oleic acid. —Glycerine.—Drying oils.	302
Tallow	309
Palm oil. — Method of obtaining palm oil. — Palmitin.—Palm oil trade.—Methods of bleaching palm oil by bichromate of potash ; by chlorine ; by heat ; by heat and air ; and by nitric acid.	310
Rosin	319
§ III. MANUFACTURE OF HARD SOAP	321
Unctuous matters employed in making white soap	321
Composition of white soap	321
Details of the process of making white soap.—Comportment of soap with a solution of salt.—Method of making hard soap in Germany.—Soap frames.—Crutching.	322
Mottled soap	327
Silicated soap	329
Yellow soap	329
Transparent soap	331
§ IV. MANUFACTURE OF SOFT SOAP	331
Consumption of soap in Great Britain	334

	PAGE
Comparison of the progress of the consumption of soap with that of other articles and the population from 1831 to 1841 . . .	335
Arguments against the soap duty	336

VII. SULPHUR AND SULPHURIC ACID.

§ I. SULPHUR	338
Views of ancient chemists on the nature of sulphur.—Native sulphur.—Iron pyrites as a source of sulphur.—Processes for obtaining sulphur from sulphuretted hydrogen and sulphurous acid.—Refining of crude sulphur.—Properties of sulphur.—Applications of sulphur.—Sulphur trade.	338
§ II. SULPHUROUS ACID	354
Modes of preparing sulphurous acid.—Properties of liquid and gaseous sulphurous acid.—Use of sulphurous acid as an external remedial agent, and in bleaching.	354
§ III. SULPHURIC ACID	361
Original process for preparing sulphuric acid from copperas . . .	361
Nordhausen sulphuric acid.—Anhydrous sulphuric acid. . . .	362
Improvement introduced by Lefevre and Lemery.—History of the progress of the manufacture of sulphuric acid.—The manufacturing process followed twenty years since.	363
Chemical reactions which take place in the sulphuric acid process	367
Details of the mode of manufacturing sulphuric acid from sulphur	374
Manufacture of sulphuric acid from iron pyrites	381
Manufacture of sulphuric acid from sulphuretted hydrogen, soda-waste, and sulphate of lime	385
Process for making sulphuric acid without nitre	387
Concentration of the acid	389
Superiority of the modern continuous over the old intermittent process of making sulphuric acid	392
Properties of concentrated sulphuric acid	395
Hydrates of sulphuric acid	396
Testing of sulphuric acid.—Tables of Mr. Parkes and Dr. Ure, exhibiting the quantity of real sulphuric acid in diluted acid at different densities.	398
Table exhibiting the variations in density of oil of vitriol through change of temperature	402
Table exhibiting the boiling points of sulphuric acid at different strengths	403
Impurities in commercial sulphuric acid. Sulphate of lead; arse-	

CONTENTS.

xi

	PAGE
nious acid ; sulphate of tin ; nitrous acid.—Method of purifying sulphuric acid.	404
Principal applications of sulphuric acid	407

VIII. THE SODA MANUFACTURE.

Characteristic properties of alkalis	409
§ I. SODIUM, CAUSTIC SODA, AND THE CARBONATE OF SODA	411
Sodium	411
Caustic soda	412
Table exhibiting the proportion of hydrate of soda and of dry caustic soda in leys at different densities	414
Carbonate of soda	414
Sesquicarbonate of soda, mineral soda or trona	416
Bicarbonate of soda	417
§ II. BARILLA AND KELP	419
§ III. MANUFACTURE OF SODA FROM COMMON SALT	422
Invention of the common soda process by M. Leblanc	422
Materials used in the soda process.—Chemical history of common salt.—Sources of common salt.	423
Conversion of common salt into sulphate of soda by the application of sulphuric acid.—“Decomposing furnace.”—Means of condensing the disengaged muriatic acid gas.	425
Conversion of common salt into sulphate of soda by sulphate of iron, by sulphate of magnesia, and by iron pyrites	431
Conversion of sulphate of soda into crude carbonate of soda or “black-ash.”—“Fluxing furnace” or “black-ash furnace.”—Action of coal and carbonate of lime on sulphate of soda.	432
“Soda-waste”	437
Preparation of “white-ash” from “black-ash.”—White-ash furnace.	437
Soda crystals	440
Proposed modification of the soda process	443
§ IV. ALKALIMETRY	448
Object of alkalimetry.—Alkalimeter.—Mode of preparing the test-acid.—Manner of applying the test-acid to soda.—Interference of various impurities contained in soda-ash.—Manner of applying the test-acid to potash.—Valuation of carbonate of soda by estimating the amount of carbonic acid present in the carbonate.	448

APPLIED CHEMISTRY;

IN

MANUFACTURES, ARTS, AND DOMESTIC ECONOMY.

MANUFACTURE OF GLASS.

§ I. History of the Glass manufacture.—II. The properties of Glass and the principles of its manufacture.—III. Materials used in the manufacture of Glass.—IV. Details of the Manufacture.—V. Defects in Glass.—VI. Colouring materials for Glass.

§ I. HISTORY OF THE GLASS MANUFACTURE.

As a generic term, the name of *glass* has been applied to several mineral substances which liquefy, or become semi-fluid and transparent, on the application of a strong heat, and which retain their transparency or translucency when allowed to cool and solidify. If broken, after having been fused and again solidified, such bodies generally exhibit in their fracture that peculiar lustre called vitreous.

In its common acceptation, however, the name has a much more limited application; it being confined to a few members of the above class, having a saline

constitution, that is, consisting of an acid on the one side, and a metallic oxide or base on the other, the acid constituent of which is silica or silicic acid, while the basic is commonly a mixture of an alkali with an earthy base, such as lime, or a mixture of an alkali with an oxide of a metal proper, such as oxide of lead.

Few productions of artistical ingenuity contribute more to our convenience and comfort than this singular and beautiful substance, the manufacture of which may be traced to a period of very remote antiquity. Nothing is known respecting the exact time of the discovery of glass, and the precise attainments of the ancients in its manufacture are also involved in uncertainty. Since no mention is made of glass in the Mosaic narrative, it has been considered that the more ancient Egyptians were unacquainted with it; but in opposition to this idea, it is urged that beads composed of glass, stained blue by a metallic oxide, have been discovered among the tombs at Thebes, and that the glaze on the earthenware beads by which some mummies are adorned is also true glass, coloured in a similar manner. The passage in the Book of Job, in which mention of glass occurs (ch. xxxvii. v. 18), is not generally considered a proof of the remoteness of its origin, as the Hebrew word which has been rendered *glass* in the Vulgate and Septuagint, has been differently translated in other versions, being used to signify various bodies possessed of lustre and transparency.

The art of making glass undoubtedly originated in hazard observations and experiments. Some operations practised in the ancient arts, such as the

firing of earthen vessels, and the reduction of metals from their ores, in which vitrifiable materials are exposed to an intense heat, were well calculated to lead to the invention. But these same operations have been practised by the Chinese from a very remote period without giving them a clue to a practicable process for making glass on the large scale. It is said, that notwithstanding the early proficiency of the Chinese in the manufacture of porcelain was so long unrivalled in Europe, yet this people are entirely unacquainted even now with an advantageous method of making glass from the raw materials; their operations in this way being chiefly confined to the re-manufacture of broken glass of foreign production. The skill of the Chinese, however, in imitating various precious stones in vitreous materials, has long been celebrated.

The commonly received account of the discovery of glass, narrated by Pliny, seems to be unworthy of credit. According to this story, some mariners, whose ships had been driven on shore at the mouth of the river Belus which flows from Mount Carmel in Galilee, lighted a fire on the sandy shore for the purpose of cooking their victuals, supporting their kettles on lumps of *natron* or carbonate of soda; and are said to have observed that the sand, when incorporated with the alkali by heat, melted and gave rise to a mass of transparent stone. The sand obtained from the shores by the river Belus was certainly supposed, for a long time, to be peculiarly adapted to the manufacture of glass, and was consequently exported to distant countries for that purpose; but it is more probable that this circumstance

was the origin of the tradition narrated by Pliny, than that the reputation of the sand originated in the above accident.

The art of making and blowing glass was known to the Phœnicians, and the glass-works of Sidon and Alexandria enjoyed considerable reputation in the time of Pliny. From Alexandria, the Romans were supplied, at one time, with a great part of their glass vessels. It is said that the Emperor Nero paid no less a sum than 6000 sesteria (equal to about 50,000*l.* of our money) for two glass cups with handles, not remarkable for their size, but thus valued on account of their perfect transparence. The manufacture of coarse glass drinking-vessels was carried on at Rome from the time of Nero, but it was not until long afterwards that the Roman artisans attained proficiency in the art. One of the most celebrated specimens of the production of the glass-houses of antiquity is the vessel known by the name of the Portland or Barberini vase, the body of which was for a long time erroneously supposed to be formed of porcelain. This vessel was found about three centuries ago, enclosed in a marble sarcophagus, in the tomb of Alexander Severus, who died in the year 235. The body of the vase is deep blue glass, and is ornamented with delicate white opaque figures in low relief, in the style of cameos. The entire height of the vessel is ten inches, and its greatest breadth seven inches. For upwards of two centuries it ornamented the palace of the Barberini family at Rome; after which it became the property of Sir William Hamilton, from whom it passed to the Duchess of Portland. It is now deposited in the British Museum.

In the thirteenth century, the manufacture of glass was successfully prosecuted on an extensive scale at Venice, where it was probably introduced by the Crusaders, who had contrived to learn the glass-making processes of the Phœnicians during the Holy War. The quality of the drinking-glasses and mirrors manufactured at Venice has been highly extolled, and the artisans of that city continued to supply the greater part of the glass vessels required for all Europe during two or three centuries.

France was the European state in which the manufacture of glass was next conducted on a considerable scale; the Venetian processes having been introduced there, during the ministry of M. Colbert, by some French artists who had resided in Venice. Long previous to this, however, to give encouragement to the glass manufacture, the French monarch, Louis IX., declared its prosecution to be in nowise derogatory to the dignity of aristocracy; and a statute was afterwards enacted whereby none but gentlemen or the sons of nobility were allowed to establish a glass-house, or even engage in any branch of the manufacture as working artisans. A grant of a royal charter of incorporation accompanied the restriction, by which various important privileges were conveyed to the manufacturers. Traces of the feeling of the gentility of the art of glass-making might have been detected in France, and even in this country,* only a few years since; but they are now almost entirely extinct. The French artists who had learned the processes of the Venetians were establish-

* A few years ago the workmen in some British glass-works were commonly called "gentlemen glass-blowers."

ed by the Government in works at Tourlaville near Cherbourg, in the year 1665.

Until towards the close of the seventeenth century, the only method commonly practised of fashioning a lump of glass into a vessel of any form, was by *blowing*, in a manner to be afterwards described; but in 1688, the important improvement of *casting* plates of glass for looking-glasses and other purposes, was introduced by Abraham Thevart, who established a company and erected works in Paris, after having obtained a patent for working the process exclusively for thirty years. The Parisian establishment was soon discontinued, but another was erected on a very extensive scale by the same company at St. Gobin in the department of the Aisne, which continued for nearly a century to be the only place on the Continent from whence cast mirror-plates could be procured. The establishment at St. Gobin is still in existence, and is deemed one of the most extensive in Europe. It is doubtful whether Thevart is entitled to the merit of having been the original inventor of plate-glass, as St. Jerome states that in his time (A. D. 422) glass was melted and cast into plates for windows. Blancourt ascribes the invention of the method of casting glass plates to the accidental breakage of a pot containing melted glass, which flowed under a large flag-stone. On removing the stone, a part of the glass was found to be in the form of a plate, such as could not be procured by blowing; and the idea of casting being thus suggested to the artisan, he immediately afterwards proved its practicability. This accident is said to have occurred towards the end of the fifteenth century.

The glass manufacture does not appear to have been prosecuted in this country on anything like an extensive scale until the middle of the sixteenth century; but it is believed that small glass articles had been made in England at a very early period, the processes being derived, most probably, from the Phœnicians when trading to this country for tin. The glass rings termed the *glain neidyr*, or Druid glass rings, which are frequently found near Aberfraw Palace, are supposed to have been made by the Druids.

The manufacture of window-glass was commenced in England in 1557, at Crutched Friars, London; and a flint-glass manufactory was established shortly afterwards at Savoy House in the Strand. The using of pit-coal instead of wood fuel was an important improvement introduced by Sir Robert Mansell in 1635; in consideration of which he was granted, by Government, some important privileges in the manufacture.

Very little progress was made in the art of glass-making, in this country, until the year 1670, when the processes practised at Venice were introduced here by some artisans from that country under the patronage of the second Duke of Buckingham; and three years afterwards an establishment for the casting of plates of glass was set at work at Lambeth under the same auspices. Another century elapsed, however, before any establishment of magnitude was undertaken for the plate-glass manufacture. In 1771, the British Plate-glass Company was chartered by act of parliament; and the company, having subscribed a joint-stock in eighty shares of five hundred

pounds each, erected a very extensive factory at Ravenhead, near St. Helen's in Lancashire. These works, which cover about twenty acres of ground, are still in active operation, being rivalled by none but those of St. Gobin in France, now under the management of M. Tassaert.*

This brief historical sketch of the progress of the glass manufacture may be very properly concluded by the following paragraph, taken from the writings of one of the most celebrated authors of the last century.

“Who, when he saw the first sand or ashes, by a casual intenseness of heat, melted into a metalline form, rugged with excrescences, and clouded with impurities, would have imagined that in this shapeless lump lay concealed so many conveniencies of life as would in time constitute a great part of the happiness of the world? Yet by some fortuitous liquefaction was mankind taught to procure a body at once in a high degree solid and transparent, which might admit the light of the sun and exclude the violence of the wind; which might extend the sight of the philosopher to new ranges of existence, and charm him, at one time, with the unbounded extent of the material creation, and at another with the endless subordination of animal life; and what is yet of more importance, might supply the decays of nature, and succour old age with subsidiary sight. Thus was the first artificer in glass employed, though

* Some account of the establishment at Ravenhead will be found in another part of the present article.

without his own knowledge or expectation. He was facilitating and prolonging the enjoyments of light, enlarging the avenues of science, and conferring the highest and most lasting pleasures ; he was enabling the student to contemplate nature, and the beauty to behold herself."—(Rambler, No. IX.)

§ II. ON THE PROPERTIES OF GLASS AND THE PRINCIPLES OF ITS MANUFACTURE.

The general physical properties of glass are so well known as to render a description of them superfluous. Perhaps the most peculiar property of this body is exhibited when it is exposed to the action of a strong heat. Glass, like every other fusible solid, passes into a state of perfect liquidity, if heated sufficiently high ; but at a pretty wide range of temperature, inferior to that necessary for perfect fusion, this substance possesses an extraordinary degree of plasticity, ductility, and flexibility, so as to admit of being blown, moulded, drawn, or cut with a pair of scissors, into every fanciful form that can be suggested. Its ductility is such, that a small lump in this intermediate state, enclosing a little globule of air, may be drawn out into a tubular thread of several hundred feet in length in one minute. At common temperatures, and in thick pieces, glass is one of the most brittle substances known ; and in thin plates, it is equally remarkable for its almost perfect elasticity. Glass in its ordinary state is entirely devoid of the quality of malleability, which

would seem to be incompatible with that of vitrification.*

Different kinds of glass vary in specific gravity from 2.4 to 4.0. Flint-glass or crystal, which contains a considerable quantity of oxide of lead, is the most dense, its spec. grav. being from 3.3 to 4.0. Plate-glass, which contains no oxide of lead, but soda and lime, has the density 2.4 or 2.6.

It has already been observed that all the varieties of glass in common use are bodies of a saline constitution; the acid in which is silicic acid or silica, formerly called earth of flints; the basic constituents being an alkali and an earth, or an alkali and the oxide of a metal proper.

Silicic acid, when prepared from its combination with an alkali by a process which will be noticed

* "Several ancient authors (Dion Cassius, Petronius Arbiter, and Isidorus) relate, that in the reign of Tiberius, an architect, who had been banished from Rome on account of his great popularity, having in his retirement discovered the means of so far altering the nature of glass as to render it malleable, ventured to return to Rome, in the hope of securing both a remission of his sentence and a reward for his invention. This discovery not agreeing, however, with the supposed interests of the tyrant, who feared lest the value of gold might be lowered by its means, the architect was beheaded and his secret died with him. This is probably only another version of the story related by Pliny, of the same important discovery having been made by an artist in Rome, when such of the populace as imagined that their interests would be injuriously affected thereby conspired together and destroyed his dwelling.

"A similar discovery, attended by results as unsatisfactory, and which is said to have occurred in France in the more modern times of Louis XIII., is recorded by Blancourt. He says that the inventor, having presented a bust formed of malleable glass to the Cardinal Richelieu, was rewarded for his ingenuity by perpetual imprisonment, lest the 'vested interests' of French glass manufacturers might be injured by the discovery." Porcelain and Glass manufacture. Lardner's Cyclopædia, p. 131.

without his own knowledge or expectation. He was facilitating and prolonging the enjoyments of light, enlarging the avenues of science, and conferring the highest and most lasting pleasures ; he was enabling the student to contemplate nature, and the beauty to behold herself."—(Rambler, No. IX.)

§ II. ON THE PROPERTIES OF GLASS AND THE PRINCIPLES OF ITS MANUFACTURE.

The general physical properties of glass are so well known as to render a description of them superfluous. Perhaps the most peculiar property of this body is exhibited when it is exposed to the action of a strong heat. Glass, like every other fusible solid, passes into a state of perfect liquidity, if heated sufficiently high ; but at a pretty wide range of temperature, inferior to that necessary for perfect fusion, this substance possesses an extraordinary degree of plasticity, ductility, and flexibility, so as to admit of being blown, moulded, drawn, or cut with a pair of scissors, into every fanciful form that can be suggested. Its ductility is such, that a small lump in this intermediate state, enclosing a little globule of air, may be drawn out into a tubular thread of several hundred feet in length in one minute. At common temperatures, and in thick pieces, glass is one of the most brittle substances known ; and in thin plates, it is equally remarkable for its almost perfect elasticity. Glass in its ordinary state is entirely devoid of the quality of malleability, which

dinary state) in water and most other liquids, and its general indifference to chemical agents when applied in aqueous solution, the acid characters of this substance, that is, its disposition to unite with and neutralize the alkaline properties of potash, soda, and other bases, are not so obvious as those of most other substances belonging to this class of bodies; and until the researches of Sir Humphrey Davy and Berzelius, silicic acid was ranked with earths proper. Feeble, however, as are its acid characters, this substance may be made to unite with alkalies and most other bases, to form a true class of salts, of definite constitution. When a mixture of silicic acid with carbonate of soda or carbonate of potash is strongly calcined in a crucible, the alkaline carbonate is decomposed, a silicate of the alkali being formed and carbonic acid gas evolved. This decomposition is produced through the more powerful affinity of the alkaline base for silicic acid than for carbonic acid, when the materials are placed in the circumstances above mentioned. A compound of silicic acid with an alkali may also be obtained by the continued digestion of the acid, in a state of fine powder, in the aqueous solution of the alkali.

Silicic acid appears to be capable of combining with alkalies in more than one proportion, forming combinations which differ little from each other in their properties, except in degree of fusibility; those which contain the largest proportion of alkali being invariably the most fusible. But it is probable that some of these apparently definite silicates may be merely mechanical mixtures of true silicates with silicic acid, for a fused alkaline silicate possesses the property of dissolving silicic acid with a readiness proportional

to its temperature; and the silicic acid and silicate of such mixtures do not separate by crystallization, but always solidify together as a homogeneous glass. One part of potash (anhydrous) is capable of bringing into a state of fusion, in an ordinary wind furnace, even ten parts of silicic acid; which proportions correspond to fifteen equivalents of silicic acid and one equivalent of potash. With a larger proportion of potash, a white enamel, instead of a glass, is obtained. The greatest quantity of silicic acid with which one part of anhydrous soda can be made to unite readily to form a fusible glass, is twelve parts. This proportion corresponds to one equivalent of soda and twelve equivalents of silicic acid. With equal weights of the bases, soda produces a more fusible silicate than potash.

A point which deserves particular attention, is, that alkaline silicates always retain their vitreous character; they never acquire a stony appearance, nor do they become crystallized, whether cooled quickly or slowly.

The only silicates which are soluble in water are those of potash and soda. The substance called *soluble glass*, a solution of which has been applied to paper, cloth, wood, &c., to prevent or retard their inflammation on the contact of an ignited body, is, as usually made, a combination of the silicate of potash with the silicate of soda, made by fusing a mixture of silicic acid with the alkaline carbonates. The proportions of the materials recommended by Doebereiner for preparing this compound are 70 parts of carbonate of potash, 54 parts of carbonate of soda, and 152 parts of ground flints or quartzose sand.

This double silicate is more fusible than the silicate of potash alone, with a corresponding proportion of silicic acid; and the solution of the former penetrates into the pores of wood with greater facility than that of the latter. The solubility of alkaline silicates is just in proportion to the quantity of alkali they contain, those which contain most alkali being most soluble.

On the addition of a strong acid, such as the muriatic for instance, to a solution of the silicate of potash or soda, the strong acid combines with the alkali and sets silicic acid at liberty. If the solution is tolerably strong, the silicic acid disengaged in this manner is precipitated in a gelatinous state, in combination with a definite quantity of water. But if the silicic acid present forms less than one-thirtieth of the weight of the water, it is retained in solution; for though perfectly insoluble in water, in its ordinary state, this substance may be brought into a peculiar condition, in which it is soluble to a certain extent. The thermal springs of Reikum and Geyser in Iceland contain a considerable quantity of silicic acid in solution in this peculiar state, and most spring water contains a minute quantity. The gelatinous precipitate of silicic acid, obtained as just described, may be dissolved if put to digest in thirty times its weight of water; but if dried so as to expel its combined water, as well as that which served to hold it in solution, it becomes perfectly insoluble in water.

When a hot concentrated solution of silicic acid in muriatic acid is allowed to cool, it assumes the form of a tremulous, transparent jelly, of sufficient consistence to allow of the inversion of the vessel

containing it, without any flowing out. On a further desiccation the silicic acid parts with its combined water, and becomes aggregated and insoluble.

The properties of the silicates of earthy bases and of oxides of metals proper, which also enter into the composition of glass, and therefore require our examination, are quite different, in some respects, from those of the alkaline silicates.

When an intimate mixture of silicic acid and carbonate of lime (chalk or marble) is strongly calcined, combination always ensues, with the formation of silicate of lime; and if the carbonate constituted more than 36 per cent. of the weight of the mixture, the resulting mass is entirely soluble in muriatic acid. But the mass does not enter into a state of fusion unless the proportions of lime and silicic acid are confined within limits not very distant, and even in the proportions most favourable for fusion it requires the highest temperature attainable in a wind furnace for the mass to become quite liquid. The silicates of lime which contain 53, 62, and 75·5 per cent. of silicic acid are the most fusible (Berthier). The formulæ of these silicates are $\text{Ca O} + \text{Si O}_2$; $2 \text{ Ca O} + 3 \text{ Si O}_2$, and $\text{Ca O} + 2 \text{ Si O}_2$. These compounds are not vitreous, like the alkaline silicates, but stony and slightly translucent like porcelain, if they have been brought to a state of perfect fusion. Silicate of lime enters into the composition of plate-glass, window-glass, bottle-glass, and crown-glass.

It is difficult to form silicate of alumina by the calcination of a mixture of alumina and silicic acid, in consequence of the very intense heat requisite to

determine the combination. But the presence of some other bases, which form fusible silicates, greatly assists the union of the silicic acid with alumina. Silicates of alumina are found in great abundance in nature, most frequently in combination with other silicates. Clays are composed almost entirely of silicate of alumina; felspar and leucite are silicates of alumina and potash; analcime and albite are silicates of alumina and soda; prehnite, stilbite, mica, mesolite, tourmaline, and several other minerals are silicates of alumina and lime. All the proper silicates of alumina are quite infusible at the highest temperature of a wind furnace.

The variety of glass of which silicate of alumina always forms a constituent is bottle-glass.

Silicates of lead may be readily prepared by calcining in a common furnace mixtures in atomic proportions of silicic acid and oxide of lead. If the mixture contains any quantity less than four equivalents of silicic acid to one of oxide of lead, it fuses readily; oxide of lead imparts fusibility to all silicates infusible by themselves, if applied in sufficient quantity.

Silicate of lead forms an essential constituent of flint-glass, crystal, and the kind of glass called strass. An excess of oxide of lead gives the glass a yellowish tint.

Protoxide of iron forms several definite compounds with silicic acid, some of which are met with in nature. Mixtures of silicic acid with the protoxide in proportions corresponding to the following formulæ, $4 \text{ Fe O} + \text{Si O}_2$, $2 \text{ Fe O} + \text{Si O}_2$, $\text{Fe O} + \text{Si O}_2$, and $2 \text{ Fe O} + 3 \text{ Si O}_2$, may be fused in a wind furnace;

black or dark olive-grey compounds are thereby formed, all of which possess a crystalline or lamellar structure, with the exception of $2 \text{ Fe O} + 3 \text{ Si O}_2$, the fracture of which is conchoidal (Berthier). The dark colour of common bottle-glass is chiefly owing to the presence of one of the silicates of the protoxide of iron; and the first three of the above silicates are the basis of the slags of iron blast furnaces, in which they are often found in the state of regular crystals.

M. Berthier could not succeed in forming a silicate of peroxide of iron by igniting a mixture of the peroxide with silicic acid. After exposure to a very intense heat, the mixture still remained in a pulverulent state, without any combination having taken place. In the presence of an easily fused silicate, peroxide of iron forms a greenish yellow compound with silicic acid.

The silicates of protoxide of manganese formed artificially by heating carbonate of manganese with silicic acid, are fusible, crystalline, and coloured either slightly red, green, or olive.

From the preceding brief description of the properties of all the silicates of which the common varieties of glass are composed, it appears, that neither of them separately is fit to make glass intended to bear exposure to the weather. The essential qualities required in common glass are transparency, absence of colour, moderate fusibility, and insolubility in water, which qualities are never found combined in a single silicate.

Among this class of bodies, permanent transparency and solubility in water are possessed only by

silicates of the fixed alkalies, potash, soda, and lithia: all the remaining silicates, not excepting silicate of lead when it does not contain an excess of oxide of lead, are either perfectly opaque or translucent like porcelain, and quite insoluble in water, and most of them have a crystalline structure. Here we have the principles of a distribution of all simple silicates into two classes, which will be found of great convenience when considering the practical application of these bodies more in detail.

But although no simple silicate can be used as glass, for the reasons just mentioned, yet mixtures of different silicates may be obtained fulfilling all the required conditions. When a mixture of two silicates belonging to the opaque or crystalline class is strongly calcined, combination sometimes ensues, with the formation of a true double salt, the properties of which are not always the mean of those of its constituents. Such double silicates are generally more fusible and more translucent than their constituents separately. But no combination consisting of two opaque or translucent silicates only can be obtained artificially in a state of transparency; nor can a perfectly insoluble glass be prepared from mixtures in any proportions of the fixed alkaline silicates only.

From this class of bodies a combination of the qualities of transparency and insolubility in water, with absence of crystalline structure, can only be obtained (with a single exception),* by combining together silicates belonging to the different classes above referred to; and as such a combination, every ordi-

* The exception referred to is the silicate of oxide of lead, containing an excess of base. This substance forms a transparent but yellow glass.

nary variety of transparent glass may be considered. The earthy or metallic silicate thereby loses its opacity, and in a great measure its disposition to crystallize; while the alkaline silicate, on the other hand, becomes rendered insoluble. The temperature at which the combination of the two silicates softens or fuses is also much more convenient for working than that necessary for the fusion of the earthy or metallic silicate alone.

Potash or soda, or a mixture of both of these alkalis, forms an essential constituent, therefore, of all the common kinds of glass: the differences in the properties of the various kinds are principally produced by varying the quality and the proportion of the base of the earthy or metallic silicate. Considering glasses as true chemical, and therefore definite, combinations of different silicates, the various kinds may be distributed under the following heads:

1. Silicate of potash and oxide of lead ;
2. Silicate of soda and lime, or silicate of potash, soda, and lime ;
3. Silicate of potash and lime ;
4. Silicate of soda, lime, alumina, and oxide of iron.

To the first class belong flint-glass, crystal, and strass; flint-glass contains more oxide of lead than crystal, and strass more than flint-glass.

Common window-glass, English crown-glass, and plate-glass constitute the second class in the above arrangement.

Foreign crown-glass and the refractory Bohemian glass are the double silicate of potash and lime.

The fourth class comprises the coarse green glass of which wine-bottles are made.

It is uncertain whether glass ought to be considered a chemical combination, or a mere mechanical mixture of the different silicates. A circumstance highly favourable to the view of its being a definite chemical compound, is, that the nearer the materials for the glass are compounded in atomic proportions, the better, in general, is the quality of the glass, other circumstances of the manufacture being equal. If an excess of the alkali is introduced, a portion of the excess volatilizes when the mixture is fused, and the resulting glass affords to boiling water a small quantity of the alkaline silicate, much more readily than it would had the materials been compounded in proportions rigorously atomic. The power of glass to resist the continued action of boiling water and acid and alkaline liquids may be ascertained by boiling concentrated sulphuric acid upon the glass: if good, the surface remains smooth and transparent; but if bad, it becomes rough. The only acid which acts upon glass with energy is the hydrofluoric.

If a moderately thick glass vessel is cooled to the ordinary temperature soon after it is formed, the brittleness of the glass is increased to such an extent that a small change of temperature or the merest scratch is apt to cause the vessel to fly to pieces. The two philosophical toys known as the Bologna phial and Prince Rupert's drops, and the "tests" or "proofs" which may be obtained at the flint-glass works, are well adapted for illustrating the properties of glass in this peculiar condition. The first of these is a common-shaped phial with a thick bottom and thin sides, which has been cooled to the ordinary

temperature immediately after being blown. If a small piece of any hard and angular mineral capable of abrading glass, such as a grain of sand, or what is better, a fragment of a gun-flint, is dropped into the phial, the latter immediately falls to pieces, the fracture commencing from the part abraded. The phial, however, will sustain a heavy blow with a wooden mallet, or the concussion caused by the fall of a leaden bullet, without injury. Prince Rupert's drops are small, solid, pear-shaped pieces of quickly cooled glass with an elongated stem, made by allowing the red-hot glass to drop into cold water. The spherical part of the drop will bear without injury a heavy blow from an instrument the surface of which is not sufficiently hard to scratch the glass; but if the minutest portion of the stem or tail is broken off, the whole drop instantly falls into a multitude of small fragments; and if the drop is held by the fingers, a slight stinging sensation is perceived from the sudden rupture.

These remarkable properties of quickly cooled glass are not difficult of explanation; they are produced merely by the unequal contraction of different parts of the same vessel through an unequal rate of cooling. Owing to the imperfect conducting power of glass, the surface of the vessel in contact with the atmosphere becomes cooled and solidified while the interior substance remains in the soft and expanded state. When quite cold, the glass is therefore in a state of tension, the relative positions of the exterior and interior portions not being exactly the same as if the whole vessel had been allowed to contract equally by a very gradual cooling. In this state of tension,

which has been compared to that of a piece of cloth stretched unequally in different parts, the slightest scratch on the surface is sufficient to derange the equilibrium; a fracture consequently ensues, which, from the elastic quality of the glass, proceeds through the entire thickness of the vessel.

The glass may obviously be prevented from acquiring these properties by subjecting it to a slow refrigeration, commonly called "annealing," so that the contraction of the interior and exterior portions may be as equable as possible. The disposition of badly annealed glass vessels to fly to pieces may even be completely corrected long after the vessel is become quite cold, by heating it slowly to a temperature about that of boiling water and then allowing it to cool very gradually. If heated to redness and slowly cooled, the Bologna phial and Prince Rupert's drops may be entirely deprived of their extreme susceptibility of breaking. The glass experiences an increase in density by this treatment, which shews that an approximation of the particles takes place.

If glass is maintained for a long time, however, at a high degree of heat, but lower than that requisite for its fusion, it is apt to suffer another change in its molecular structure; becoming opaque or translucent, fibrous, considerably harder, more difficult of fusion, a conductor of electricity, and a better conductor of heat. After being thus treated, the glass is so hard as to cut common glass with facility, and to give sparks when struck with steel; it is incapable of becoming electrically excited by friction, unless insulated; and if the heating has been con-

tinued a long time, the glass is enabled to sustain without breaking a sudden cooling from a red heat to the ordinary temperature, by being plunged into cold water. Several interesting observations on the properties and uses of glass in this devitrified state were made by the French naturalist, M. Reaumur, and communicated to the Academy of Sciences in 1739. The opaque glass is commonly known as "Reaumur's porcelain."

All the varieties of true glass are probably subject to this change in their molecular structure, but some kinds are much more susceptible of it than others. The glass which acquires it with the greatest facility is the common green bottle-glass, which differs from the other varieties in containing a greater number of bases. It was formerly believed that the change produced in the glass is owing to the chemical action of the powdered gypsum or sand with which it is necessary to surround the vessel in order to preserve its shape, the powder being supposed to act by a process like that distinguished by the name of cementation. But the devitrification of the glass proceeds as regularly forward in the absence of gypsum, sand, or any other cementing substance; it must be effected, therefore, by the action of heat alone. The glass sometimes experiences, however, a slight change in its composition, during the prolonged heating, through the volatilization of a trace of its alkali; but the loss of alkali is by no means an essential part of the process of devitrification, as is believed by some. The bases in the glass assume a new molecular arrangement; and the silicates, instead of continuing in a vitreous state, become crys-

tallized and opaque. The higher the temperature to which the glass is exposed, provided it is below the point at which fusion takes place, the more rapid is the change. At a full red heat, a piece of a common wine-bottle has been completely devitrified in two hours. The toughness of the altered glass, its difficult fusibility, and its power of withstanding the action of acid liquids and of resisting sudden alternations of temperature, would probably render vessels of this material of great service in the laboratory as a substitute for those of ordinary glass, porcelain, and even in some cases, for those of platinum.

If the devitrified glass is exposed to a very intense heat, it fuses and reassumes its original vitreous characters, which it retains permanently if cooled in the ordinary manner. The farther the process of devitrification had been carried, the higher is the temperature necessary for fusion.

§ III. ON THE MATERIALS USED IN THE MANUFACTURE OF GLASS.

The quality of glass depends in a great measure on the judgment with which the ingredients from which it is prepared are selected, and on the proper application of certain correctives for the impurities that may be present. The only essential constituents of all the common kinds of glass are silicic acid, potash, soda, lime, oxide of lead, alumina, and oxide of iron; but some of these may be introduced in several different forms, in his choice of which, the manufacturer is guided in a great measure by the relative

facility with which they may be procured. The principal materials used in the fabrication of different kinds of glass are the following :

- Fine white sand ;
- Common river sand ;
- Quick-lime ;
- Lime, slacked by exposure to the air ;
- Chalk ;
- Pearlash ;
- Potashes ;
- Soda crystals ;
- Carbonate of soda, by treating common salt with pearl-ash ;
- Soda ash ;
- Sulphate of soda (salt-cake) and charcoal ;
- Common salt ;
- Broken glass ;
- Nitre ;
- Soap-boilers' waste ;
- Sulphate of potash and charcoal ;
- Red lead ;
- Litharge ;
- Black oxide of manganese ;
- Arsenious acid.

The most convenient form in which silicic acid can be procured is as fine sea-sand, which consists of minute grains of quartz rounded by attrition. The sand preferred for making the finer qualities of glass is obtained from Alum Bay, on the western coast of the Isle of Wight, and from the port of Lynn in Norfolk. A very excellent sand is also raised on the estate of the Earl of Derby, near Liverpool. For some purposes, the sand requires to be calcined, sifted, and washed.

Common flints, calcined and ground, were formerly used in the manufacture of the best glass, but that material has been entirely superseded in this country by sand. Oxide of iron is the most important of

the impurities which sand is likely to contain, a very minute quantity of the protoxide being sufficient to communicate a sensible greenish tinge to the glass.*

Lime is introduced in the forms of chalk, quick-lime, and the mixture of hydrate and carbonate of lime obtained by allowing quick-lime to slack by exposure to the air. Common chalk is not well adapted for the purpose, in consequence of the presence of a small quantity of organic matter, which imparts a brownish tinge to the glass. All the chalk used at a crown-glass house in the North of England is procured from the cliffs of Dover. The quantity of chalk or lime should be carefully apportioned to that of the other materials, as a slight excess is apt to produce a milkiness in the glass, through the separation of a portion during the cooling. Soda-glass bears a greater addition of lime than potash-glass.

* Two methods of preparing pure silicic acid for the glass manufacture from common sand or any impure siliceous mineral, have been proposed by Mr. Ragon. One of these consists in calcining at a red heat a mixture of one part of the siliceous substance with three parts of an alkali, dissolving the fused mass in water, and decanting and evaporating to dryness the clear supernatant liquid. The residuary alkaline silicate may then be mixed with more silicic acid, and with the other constituent necessary to the production of glass. The other method consists, first, in heating a mixture of the siliceous mineral with fluor spar and sulphuric acid, and in conducting the disengaged fluosilicic acid gas (fluoride of silicon) into water. By the reaction of the water and fluoride of silicon there are obtained, a deposit of pure silicic acid in a state of most minute division, and an aqueous solution of hydrofluosilicic acid. The former is to be separated by filtration or any other convenient mode, and used in the manufacture in the ordinary manner; and the solution of hydrofluosilicic acid is mixed with common salt and evaporated to dryness in order to obtain dry fluosilicate of soda, which it is said may be used as one of the materials for the production of glass. For these and other "improvements" in the glass manufacture (some of which are elsewhere alluded to in this article) Mr. Ragon obtained a patent in 1839.

The presence of magnesia in the lime renders the fusion of the glass considerably more difficult.

Potash and soda are generally introduced in the form of carbonates. During the calcination with silicic acid, the alkaline carbonate is decomposed, its carbonic acid escaping in the gaseous state, while the base unites at the same time with the silicic acid.

The quality of the glass is much affected by the degree of purity of the alkali. For making fine flint-glass, the pearlash met with in commerce requires to be freed from its impurities by being digested in a very small quantity of hot water, in which the pure carbonate of potash dissolves, leaving the less soluble impurities, which are chiefly chlorides of potassium and sodium and sulphate of potash, undissolved. The solution of the carbonate is conducted into a leaden pan to cool and become clear, and is afterwards transferred to an iron boiler in which it is evaporated to dryness. For the coarser glasses containing potash, the alkali is introduced either as common pearlash or as crude potashes.

The soda used in the plate-glass manufacture is the purest that can be procured. At the celebrated establishment of St. Gobin in France, before alluded to, pure carbonate of soda is employed, prepared in the usual manner by decomposing sulphate of soda with lime and charcoal. Formerly, the greater part of the alkali used at the plate-glass works at Ravenhead was obtained by mixing common salt with a solution of pearlash; when double decomposition takes place, with production of chloride of potassium and carbonate of soda. By evaporating the mixed solution at a moderate heat, the chloride of potassium,

which is much less soluble than the carbonate, may be separated almost perfectly by crystallization; and to obtain the carbonate, the mother-liquor is afterwards evaporated to dryness.

The alkaline ingredient used in the window-glass manufacture is chiefly soda-ash, which contains, besides carbonate of soda, some chloride of sodium and sulphate of soda. For making wine-bottles, the crudest alkali that can be procured is generally employed; such as the soap-boilers' waste, which consists principally of lime that has been employed for making caustic ley. The residue of the evaporation of the mother-liquor obtained in the process of making soda crystals is also made available in the manufacture of some kinds of glass.

The alkaline sulphates have been substituted for the carbonates in some branches of the glass manufacture; but silicic acid, of itself, is scarcely able to expel the sulphuric acid of these salts. To assist their decomposition, it is necessary to introduce either charcoal, or else a larger proportion of lime or chalk than would otherwise be employed. The excess of lime or chalk acts by withdrawing sulphuric acid from the alkaline sulphate to form sulphate of lime, which does not dissolve in the fused vitreous mass, but falls as a sediment to the bottom; and if the lime is added in a proper proportion, the glass made in this way does not contain a trace of sulphuric acid. The decomposition of the alkaline sulphate is effected more easily by chalk than by lime.

In contact with charcoal at a high temperature, the alkaline sulphates are readily decomposed by silicic acid; the sulphuric acid being decomposed by

the carbon, with production of sulphurous acid and carbonic oxide gases. An excess of charcoal should be carefully avoided, as it communicates a brownish or sometimes a greenish-blue tinge to the glass. The latter colour is probably derived from some compound of sulphur with soda or sodium, analogous to that contained in the mineral lapis lazuli or the pigment ultramarine. For decomposing sulphate of soda, the proportion of charcoal should not exceed one part to thirteen of the calcined sulphate.

Another form in which soda has been introduced is that of chloride of sodium or common salt; but as silicic acid is unable, alone, to unite with the base of this compound, it is necessary to add some carbonate of potash, by the reaction of which on chloride of sodium there result carbonate of soda and chloride of potassium. The former is immediately acted on by the silicic acid, while the latter separates as a scum on the surface of the fused mass. This process is only followed on some parts of the Continent where carbonate of soda is not easily procured.

In making flint-glass, a part of the potash is introduced in the form of nitre; but that article is used, chiefly, for the purpose of destroying, by its oxidizing power, any carbonaceous matter that may exist in the ingredients, and of peroxidizing any iron which may have contaminated the sand or alkali. Nitre gives off a large quantity of oxygen gas long before the mixture attains the softening heat.

The protoxide of lead, which always enters very largely into the composition of flint-glass, is applied either as red lead or litharge. When red lead is used, a quantity of oxygen gas is disengaged during

the calcination of the ingredients; but this effect does not take place with litharge, which is the protoxide. Great care should be taken to ensure the absence of any copper and zinc in the red lead or litharge, as oxide of copper renders the glass green, and oxide of zinc milky-white. White lead (subcarbonate of lead) and galena (the native sulphuret of lead) have been occasionally employed in the place of red lead or litharge. Sulphate of lead, which may be obtained at a cheap rate in some localities and perfectly free from copper, has been proposed as another substitute. It is said that this compound readily produces a glass with silicic acid. An excess of oxide of lead impairs the brilliancy of the glass, renders it very soft, and gives it a slight yellowish tinge.

A material in common use for the preparation of most kinds of glass is old broken glass, technically known by the name of "cullet." In consequence of the volatilization of a portion of its alkali, glass cannot be worked at so low a temperature the second time as the first; for which reason it is a common practice to introduce a small excess of alkali with the cullet.

The only important material used in the glass manufacture which remains to be noticed is the black oxide of manganese. This substance is not used to impart an essential constituent to the glass, but to clear the mass of the colour which it acquires through the presence of carbonaceous matters and protoxide of iron. When the green silicate of the protoxide of iron, dissolved in the melted glass, comes into contact with one of the higher oxides of manganese, it abstracts some of the oxygen of the latter,

and becomes converted into the silicate of the peroxide of iron, which is almost colourless in comparison with the silicate of the protoxide. By thus parting with oxygen, the peroxide of manganese becomes reduced to the protoxide, which combines with silicic acid to form a colourless silicate. The carbonaceous matters which tinge the fused mass are also oxidated by the peroxide of manganese, their carbon being converted into carbonic oxide and carbonic acid gases. This application of peroxide of manganese long since procured that substance the name of "glass-makers' soap."

But if the manganese is applied in a minute quantity more than is absolutely necessary to remove the carbonaceous matters and peroxidize the protoxide of iron, it imparts a very decided lilac or amethyst colour to the glass; and with a little larger proportion the glass might be made so dark as to appear quite black when in mass. The colour of the glass in this case is due to the formation of a compound of silicic acid with the sesquioxide of manganese,* which dissolves in the fused vitreous mass. If a small quantity of charcoal or any carbonaceous substance is introduced into the melted glass, thus coloured, the sesquioxide of manganese becomes gradually reduced entirely to the state of protoxide, and the lilac colour disappears completely. The purple tinge arising from an excess of manganese is sometimes destroyed in this way on the large

* The sesquioxide of manganese is intermediate in composition between the protoxide and peroxide. The three oxides are represented by the following formulæ: protoxide = Mn O , sesquioxide = $\text{Mn}_2 \text{O}_3$, and peroxide = Mn O_2 .

scale, a wooden rod being thrust down into the melted glass; but a much more advantageous method is to introduce a small quantity of white arsenic (arsenious acid), which reduces the sesquioxide of manganese to the state of protoxide, becoming, itself, converted into arsenic acid. A very slight excess of manganese, however, is preferred by some manufacturers, as the brilliancy of the glass is considered to be increased by the delicate amethyst tint.

If a small quantity of nitre is introduced into melted glass containing the colourless protoxide of manganese, the latter acquires oxygen and becomes converted into the amethyst sesquioxide. Such a change also takes place slowly when glass containing the protoxide of manganese is exposed to air and light at common temperatures.

Another material used to destroy the brown colour arising from the presence of carbonaceous matter in the fused mass is arsenious acid, the use of which in removing the lilac tint from an excess of manganese has just been alluded to. In producing these two decolorizing effects, the action of arsenious acid is of a very different nature; it being oxidizing in the one, and deoxidizing in the other. The carbonaceous matter is dissipated in the form of carbonic oxide and carbonic acid gases; the arsenious acid becoming reduced to metallic arsenic, which is expelled in the state of vapour. The arsenic, however, should be employed with moderation, as a very small excess is apt to render the glass slightly opalescent.

§ IV. DETAILS OF THE MANUFACTURE OF GLASS.

The glass-house in which the processes of melting and blowing are performed is usually built in the form of a truncated cone, open at top, of sixty or eighty feet in height, and forty or fifty feet in diameter at the base. In the centre of the area is situated the furnace, containing from five to ten glass-pots or crucibles for melting the materials. The grate of the furnace is nearly on a level with the floor of the glass-house; and the ash-pit is a subterranean passage, extending from each side of the furnace to the exterior of the building. But the particular arrangements of the glass-house and the construction of the furnaces are varied according to the kind of glass prepared.

The glass-pots of the bottle and crown glass houses usually have the form of a truncated cone, the narrow end being the base. Their depth is commonly four feet six inches; their diameter at top from four feet to four feet six inches, and their diameter at bottom about three feet four or six inches. The pots for flint-glass are covered at top, and have a mouth at the side; but those for crown-glass and bottle-glass are open at top.

The material of which the glass-pots are made is fine clay, as pure and refractory as can be obtained. It should be free from every trace of lime, in any state, and iron pyrites; and the less oxide of iron the better. The kind of slate-clay dug out of the coal formation near Stourbridge, which contains very little, if anything, besides silicic acid and

alumina, is decidedly preferred to all other clays found in this country. After having been picked, ground, and finely sifted, the powder is mixed with about one-fourth of its weight of ground old pots, and the mixture is kneaded with water until it becomes a uniform and smooth paste. The kneading is best performed by treading with the naked feet, the mass being turned over occasionally, that every portion of it may be thoroughly acted on. The mixture is usually kept for some time in a damp cellar to "ripen," before it is worked up into shapes. After the glass-pot is formed, it is allowed to remain for a considerable time in an apartment heated by a flue to a little above the ordinary temperature (about 80°), in order that it may be slowly dried in an equal manner throughout its whole thickness. The time allowed by some manufacturers for this gradual desiccation is two or three years.

Before the pot is "set" in the furnace, it must be subjected to an annealing process, which consists in gradually increasing its temperature during several days to bright redness. This is usually done in a reverberatory, constructed for the purpose; the fire in which must be raised very slowly, not more than a shovel-full of coals being introduced at a time, and that at regular intervals. While at a bright red or even a white heat, the pot is quickly transferred, with the assistance of adequate machinery, into its seat in the hot furnace; a part of the face of which must be pulled down to allow of the ready extraction of the old pot and introduction of the new one. The duration of the pots of the crown-glass works is generally about three months.

1. FLINT-GLASS.

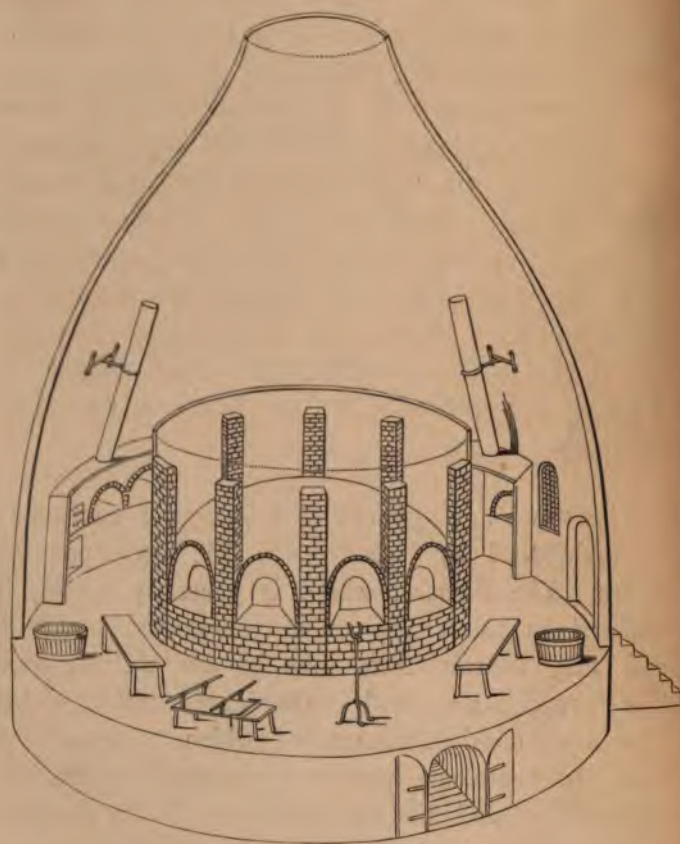
Flint-glass, the silicate of potash and lead, is distinguished from all the other kinds of true glass by its greater density, softness, fusibility, lustre, and refractive power. It is also the kind of glass most easily fashioned into vessels, but the materials from which it is prepared are considerably more expensive than those for making any other.

The glass known on the Continent by the name of *crystal* is generally made of the same materials as flint-glass, the only difference consisting in the latter having a little more oxide of lead than the former. This kind of glass derives its English name from the circumstance that calcined flints were formerly employed as its siliceous ingredient; but this use of that mineral has long since been abandoned, wherever the operations are conducted on an extensive scale.

The usual arrangement of a flint-glass house may be understood by reference to the accompanying figure. The furnace, which is generally round, is situated in the centre of a cone-shaped building, and may contain from four to ten melting-pots. The furnace represented in the figure contains eight. The flues of the furnace, of which there are as many as there are pots, are arranged at regular intervals around the circumference of the furnace, one being placed between two pots; and immediately abreast of each pot, and between two flues, is an aperture called the "working-hole," for the intro-

duction of the raw materials and the extraction of the plastic glass. At the left-hand side of the figure is represented one end of a long gallery called the "leer" or "annealing arch," in which the vessels are annealed. The small furnace at the back, on the right-hand side, is for the purpose of soften-

Fig. 1.



ing the glass during its fabrication into a vessel, when the lump is too large to be heated before one

of the working-holes. The flue for this furnace and that of the stove belonging to the annealing arch may consist of a sheet-iron tube. The opening at the base of the building represents one extremity of the vaulted ash-pit, which runs through the entire breadth of the house. The crucible for making flint-glass is of the shape shewn in fig. 2, and is often sufficiently large to contain a ton of melted glass.

Fig. 2.



Considerable difference may be found between the proportions of the materials for making flint-glass employed by different manufacturers, and it is probable that exactly the same receipt is followed in no two houses; hence a scrupulous adherence to any particular ratio cannot be considered as essential to the success of the process. A specimen of English flint-glass, of first-rate quality, analyzed by M. Berthier, consisted of

Silicic acid	59.2
Oxide of lead	28.2
Potash	9.0
Oxide of iron and manganese	1.4

This result corresponds with the following atomic constitution:

20 equivalents of silicic acid	620	59.2
3 equivalents of oxide of lead	333	31.8
2 equivalents of potash	94	9.0
	<hr/>	<hr/>
	1047	100.0

The following proportions were long ago recommended by M. Loysel, the fuel employed being coal:

Fine white sand	100	parts
Red lead	80 to 85	"
Pearlash	35 to 40	"
Nitre	2 to 3	"
Manganese	0·6	"

The mixture used by most manufacturers of the present time does not deviate greatly from the above. With a coal fire, the following may be taken as the average:

White sand	9	parts
Red lead or litharge	6·5	"
Pearlash with a little nitre	4·5	"

A very good glass may be obtained, however, with a much smaller proportion of litharge, but a higher temperature is then required for working the glass. A mixture of this kind recommended by an excellent authority (Mr. Aikin), is,

White sand	120	parts
Purified pearlash	40	"
Red lead or litharge	35	"
Nitre, with a small quantity of manganese ...	13	"

When flint-glass of a first-rate quality is required, purified carbonate of potash is always employed instead of pearlash.

The raw materials having been thoroughly incorporated together are mixed with from a fourth to a third of their weight of broken flint-glass, and the mixture is introduced, by means of a clean iron shovel, into the melting-pot, previously heated to whiteness. The raw materials for other kinds of glass are sometimes subjected to a calcination, termed "fritting," before they are introduced into the cru-

cible; but this operation is always omitted in making flint-glass. The crucible is at once filled with the mixture, and the temperature of the furnace is soon raised to the maximum. As the mass subsides by being melted, a fresh quantity of the mixture is introduced, until at length the crucible becomes filled with the melted glass. The mouth of the crucible is then closed by applying a lute of clay around the stopper, leaving only a small aperture at the bottom.

The glass does not become transparent for some time after it has attained a state of complete fusion; its opacity being due to the presence of saline and earthy impurities, which do not fuse and incorporate with the vitreous mass. Some of the infusible matters, being specifically heavier than glass, subside to the bottom of the pot; but the greater part of the saline impurities rises as a scum to the surface of the melted glass. As the scum, which is known by the name of "glass-gall" or "sandiver," rises, it is skimmed off through the aperture in the mouth of the crucible: if not removed in this way, it would be slowly volatilized as a dense vapour, and produce an injurious effect on the roof of the furnace. Every portion of this saline matter should be removed before the glass is withdrawn from the crucible for use.

When from forty to forty-eight hours have elapsed from the time of charging, the vitrification is generally complete; and if the glass-gall is entirely dissipated, and the mass become transparent and colourless, the temperature of the crucible is then lowered by lessening or altogether stopping the draught of the furnace. The object of this is to bring the glass from a state of perfect fluidity, in

which it could not be freely worked, to that peculiar plastic condition in which it is capable of being pulled, bent, blown, or cut into every conceivable shape without breaking or parting with its adhesiveness. The glass should be kept in this state all the time it is worked, which may vary from six to twenty-four hours.

Although the manual operations of fashioning various articles of flint-glass are varied almost indefinitely in their details, according to the particular form required, they are reducible, nevertheless, to a few simple processes, some of which may be illustrated by an account of the manner of producing a small bell-shaped jar. The implements of the glass-blower are few and extremely simple. The most important one is an iron tube, open at both ends, from four to five feet in length, with a bore of from one-third of an inch to an inch in diameter. A mass of the soft glass is collected on one extremity of this tube or blow-pipe, by alternately dipping the end of the pipe in the glass and exposing it for a moment to the air, until a sufficient quantity is obtained. The pipe is then held in a perpendicular position for a few seconds, with the end to which the glass is attached downwards; and when the mass is sufficiently elongated, it is rolled on a smooth and flat iron plate, called the "marver,"* in order to give it a cylindrical form. The workman now blows strongly through the tube, to cause the lump of glass to be distended by its plasticity and the pressure of

* Corrupted from the French *marbre*. The English names of several implements used in glass-houses are clearly derived from their French names.

the breath into a hollow globe (fig. 3). When a vessel of moderate size is required, it seldom happens that the globe is obtained sufficiently large and thin by a single blowing; and as the expanded glass

Fig. 3.



Fig. 4.



presently solidifies, it becomes necessary to soften it by the application of heat previous to the second blowing (fig. 4). The alternate heating and blowing are continued until the globe is obtained of a convenient size and thickness.

At this stage of the process, an assistant applies to the surface of the globe, at a place immediately opposite to that at which it is attached to the tube, a knob of soft glass on the end of a solid iron rod called the "punto" or "pontil," considerably smaller than the tube used for blowing. The two soft masses thus becoming firmly welded together, the first workman detaches the globe from the tube by touching its tubular neck either with a file or an iron rod just before wetted with cold water. After a crack has been thus produced, a smart stroke on the tube readily separates the globe, which must then be held by the punto.

Having once more softened the vessel by holding

it at the mouth of the furnace, the workman proceeds to expand the aperture left by the removal of the tube; for which purpose, his principal instrument is one resembling a large iron forceps, called a "procello," the two blades of which are connected

Fig. 5.



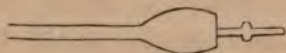
by an elastic bow, like those of a pair of sugar-tongs. With this instrument the workman, being seated on a stool provided with straight projecting arms, as shewn in fig. 5, enlarges or contracts the glass vessel as may be desirable, running the pontil at the same

time on the arms of the stool. The superfluous glass is cut away with great facility by a large pair of scissors.

When the vessel is fully formed and become quite solid, it is detached from the punto in the same manner as it had previously been detached from the tube, and is immediately conveyed to the annealing arch to undergo a very gradual refrigeration, the reasons for which have already been adverted to.

The mode of fashioning a common wine-glass will also afford a good example of the ordinary manipulations of the glass-blower. A small bulb, of the form shewn in fig. 3, having been blown, its extremity is flattened by revolving it on the arms of the stool, against a small disc of iron, and an assistant applies to

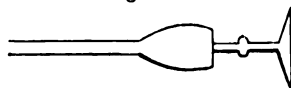
Fig. 6.



the flattened end a little lump of soft glass, which is elongated by the procello so as to form the leg of the wine-glass (fig. 6). While this is being done, the assistant blows a smaller

bulb on another tube, and applies its end, while yet soft, to the soft extremity of the leg; the small bulb is then detached from its tube, and after having been softened by exposure to a hole in the furnace, is expanded by the pro-

Fig. 7.



cello into a flat foot (fig. 7). A punto tipped with

melted glass is next ap-

plied to the centre of the foot, the blow-pipe is detached, and the body of the glass is fashioned to the required shape in the manner described above for the bell-jar. An endless variety of forms may be obtained by the dexterous combination and modification of the manipulations above alluded to.

Imitations of cut-glass vessels are made by blowing the soft glass into a polished metallic mould, the form of which it acquires with as much faithfulness as wax.

The annealing arch is a rectangular arched chamber of from thirty to forty feet in length, three feet in height at the centre, and about four feet in width. One end of the chamber is moderately heated by a small stove, the smoke and hot air from which pass along the gallery to about two-thirds of the length of the latter, where they are discharged by a chimney. The vessels to be annealed are introduced into the arch at the heated end, being disposed on shallow iron trays, called "leer-pans," which are usually placed in two rows on the floor of the chamber; and as one of the trays is removed at the cool end, another empty one to receive more hot glasses is introduced at the heated end.

The time required for properly annealing small and thin vessels of flint-glass is from twenty to twenty-four hours. As thick vessels require a much longer time, and also a higher temperature at the heated end, than thin vessels, it is usual to have two or three of these annealing galleries attached to the same working furnace, so that the process may be conducted, if necessary, in a different manner with different articles, at the same time without interruption.

The variety of glass known by the name of *Strass*,* which is used as a general colourless basis for factitious gems, on account of its remarkable lustre, belongs to the same class of vitreous bodies as flint-glass. The chief difference between the composition of strass and flint-glass consists in the former containing the largest proportion of oxide of lead. Some manufacturers also introduce a small proportion of borax. With the basis alone, by being worked on the lapidary's wheel, excellent imitations of colourless diamonds may be obtained; and by uniting it by fusion with various metallic oxides, a great variety of precious stones are counterfeited.

Great regard should be paid to the state of purity of the materials from which strass is prepared. The presence of oxide of tin in the litharge or red lead, and of oxide of iron in the sand, should be particularly avoided, as the former would communicate an opacity, and the latter a yellowish or greenish colour, to the glass. To ensure the absence of oxide of iron in the sand, that material should be calcined and

* So called from the name of its German inventor.

then washed, first with dilute muriatic acid, and afterwards with clean water.

M. Lançon, who has made several experiments on this subject, recommends the following proportions of the materials: litharge, one hundred grains; white sand, seventy-five grains; and pure carbonate of potash, ten grains. According to M. Doualt Wieland, an excellent strass may be obtained by either of the following recipes:

	No. I.	No. II.
	<i>grains</i>	<i>grains</i>
Rock crystal, ground,	4056	3456
Red lead	6300	5328
Pure carbonate of potash	2154	1944
Borax	276	216
Arsenic	12	6

	No. III.	No. IV.
Fine white sand	—	3600
Rock crystal, ground,	3600	—
Pure white lead	8508	8508
Pure carbonate of potash	1260	1260
Borax	360	360
Arsenic	12	—

M. Wieland observes, that both the lustre and density of the glass are increased by a tranquil and prolonged fusion, and hence recommends that the materials should remain in a melted state for twenty-four hours. The colouring metallic oxides proper for combining with this glass will be noticed in another section of the present article.*

* The vitreous basis preferred by Fontanien, in his treatise on coloured glasses and artificial gems, is prepared in the following manner: Eight ounces of pure rock crystal or flint, in powder, mixed with twenty-four ounces of carbonate of potash, are calcined and left to cool. This mixture is afterwards transferred to a basin of hot water, and treated

2. CROWN-GLASS.

Crown-glass, which is a silicate of soda and lime, as made in this country, is chiefly used for making windows. Being much more difficult of fusion, and therefore less easily worked, than flint-glass, it is not commonly fashioned, like the latter, into vessels of capacity, whether for use or ornament. Crown-glass is also much harder than flint-glass, and consequently not so well adapted as the latter for cutting and grinding.

The general arrangements of a crown-glass house are quite similar to those of a flint-glass house (fig. 1, page 36). The furnace containing the glass-pots, which is built in a rectangular form, is situated in the centre of the cone, with various smaller furnaces for secondary operations on each side; and the ash-pit, called the "cave," runs across the building, as in the flint-glass house. The centre furnace contains

with dilute nitric acid till it ceases to effervesce; when the frit is to be washed until the water comes off tasteless. The frit is now dried and mixed with twelve ounces of fine white lead, and the mixture is levigated and elutriated with a little distilled water. An ounce of calcined borax is to be added to about twelve ounces of the preceding mixture in a dry state, the whole rubbed together in a porcelain mortar, then melted in a clean crucible and poured into cold water. This vitreous matter must be dried, and melted a second and a third time, always in a new crucible; and after each melting, poured into cold water as at first, taking care to separate the reduced lead. To the last glass, ground to powder, five drams of nitre are added; and the mixture being melted for the last time, a mass of crystal will be found in the crucible of a brilliant lustre. To the strass thus prepared M. Fontanieu applied the name of Mayence base. Another mixture, recommended by the same authority, is, eight ounces of white lead, two ounces of powdered borax, three ounces of rock crystal, and half a grain of manganese. (Dr. Ure's Dictionary of Arts, &c., art. Glass-making.)

four or six pots, each sufficiently large to hold half a ton or more of melted glass. The best stone for constructing those parts of the crown-glass furnace which are exposed immediately to the fire, is a fire-stone of very close grit, procured from the neighbourhood of Newcastle. Extreme nicety is required in the proper adjustment of the blocks, as no cement whatever is employed for the interior of the furnace. The duration of a crown-glass furnace is from eighteen months to three years.

A crown-glass house requires several subsidiary furnaces, adjoining or around the inside of the cone, besides the oven necessary for annealing the glass-pots previous to their being set. Of these furnaces the first which comes into use is that called the "colcar,"* for calcining or "fritting" the materials previous to their being completely fused and vitrified. The form of the colcar is generally similar to that of an oven, the fire-place being on one side, so that the flame is enabled to reverberate from the crown of the colcar back to the materials on the sole. The area of this furnace may be from six to eight feet long, and from five to six feet wide, and the height in the middle about two feet. Four of the other subsidiary furnaces are for the purpose of softening the glass while it is being fashioned into a circular plate: the first is called the "blowing furnace," to facilitate the blowing of the glass into a large globe; the second, the "bottoming hole;" the third, the "nose hole;" and the fourth, the "flashing furnace;" the use of each of which will be presently described. Another fire-place is that attached to the annealing

* A name corrupted from the French *calquaise*.

arch. The flashing furnace is represented in elevation in fig. 13, page 53, and the annealing arch in fig. 15.

The materials at present employed for making crown-glass in this country are fine sand, chalk, and either soda-ash (crude carbonate of soda), or salt-cake (dry sulphate of soda), mixed with a little charcoal, with small quantities of black oxide of manganese, arsenious acid, and occasionally oxide of cobalt, to correct any defects in the colour of the glass owing to the presence of oxide of iron. On some parts of the Continent, where carbonate of potash is as available as carbonate of soda, the alkaline constituent is either a mixture of potash and soda or potash only. The analysis, by M. Dumas, of a specimen of crown-glass of German manufacture, afforded results which correspond to one equivalent of neutral silicate of potash with one equivalent of neutral silicate of lime; or $K O, Si O_2 + Ca O, Si O_2$. For making crown-glass, either a portion or the whole of the alkali is generally introduced in the state of sulphate, a small proportion of charcoal being added to decompose the sulphuric acid.

In consequence of the fluctuating quality of soda-ash, crown-glass manufacturers do not constantly adhere to any fixed proportions of the materials, and for the same reason are also under the necessity of determining, by analysis, the amount of real alkali in every fresh supply of ash before it is used on the large scale. The usual proportions employed when all the alkali is introduced in the form of soda-ash, are, 100 parts of quartz sand, 35 to 40 parts of chalk, a quantity

of soda-ash containing about 8 parts of soda, and from 150 to 200 parts of old broken glass or cullet. The proper proportions of arsenious acid and black oxide of manganese can be learned only by trial. The sand must first be calcined at a dull red heat in the colcar, and then be carefully sifted: the chalk is also calcined, but at a more moderate heat: the object of this operation being merely the thorough desiccation of the chalk, and not the expulsion of any portion of its carbonic acid. The sand and chalk having been thus dried and finely sifted, are thoroughly intermixed with the other materials, also dry and in a pulverulent state, and the mixture is ready to be shovelled at once into the glass-pots at a white heat.

Such is the method at present pursued in nearly all the crown-glass houses in this country. But formerly it was an universal practice to subject the mixture of the raw materials (neither of them having been previously heated) to a calcination in the colcar, or fritting furnace, where it was well stirred about with iron paddles and rakes. This practice is still followed, I believe, in some crown-glass houses.

The objects of this preliminary calcination, called the fritting, are, 1°, the expulsion of the water contained in the mixture, whether free or in chemical combination; 2°, the combustion and dissipation of the carbonaceous matters which may be accidentally present in the materials; 3°, the expulsion of carbonic acid from the chalk; and 4°, the union of the base of the alkaline carbonate with silicic acid, the carbonic acid being expelled. The last of these objects of the fritting process seems to be the most

important. When the raw mixture is introduced into the white hot glass-pot, a portion of the uncombined alkali may volatilize before it could have time to become fixed by uniting chemically with the silicic acid. The temperature of the colcar should be moderate, and raised gradually for three hours after the materials are introduced, so as to avoid the volatilization of the uncombined alkali. When the mixture acquires a pasty consistence, it should be diligently stirred about, in order to facilitate the extrication of the carbonic acid from the soda-ash, and the combustion of the carbonaceous matters which are present. Towards the end of the third hour, the temperature must be considerably raised, but not to an extent sufficient to fuse the mass; and at the expiration of the fourth hour, the process may be considered completed. While the mass is still hot and soft, it is raked out into large cast-iron trays, and cut by a spade into square cakes, which are afterwards piled away in a large apartment for use. Some crown-glass manufacturers formerly considered these frit bricks to improve with age, and therefore so conducted their operations as to avoid using the frit until it had been prepared for twelve months or longer. As already observed, however, the fritting process is now generally dispensed with, since it is found that as good glass may be prepared by merely desiccating the materials thoroughly previous to their being "founded" or melted in the glass-pot.

The pots being ready to receive their charge, they are filled with the raw mixture or the blocks of frit, and the furnace is brought as quickly as possible to its maximum temperature. As soon as the quantity

first introduced is melted down, which happens in about eight hours, another charge is thrown in ; and so on, until the pot contains a sufficient quantity of the melted glass. The vitrification of the mixture is generally complete in about eighteen hours.

As soon as the glass attains a state of tranquil fusion, the disengagement of gas having completely ceased, the temperature of the pot is gradually lowered by completely closing the draught-holes to the furnace ; the chinks in the door-places of the cave being stopped up, for this purpose, with mortar. After a few hours the glass becomes perfectly clear, some of the foreign saline and earthy matters having subsided to the bottom, and others risen to the surface ; and after the fire has been again raised a little, and the whole of the glass-gall skimmed away, the glass is ready to be worked off. To preserve a clean surface of glass, an earthenware ring, about two feet in diameter and three inches thick, (made of the same material as the pots,) is put to float on the melted glass, the surface having been skimmed immediately before. Within the ring, the surface of the glass is much cleaner than without.

The common process whereby a lump of this soft glass is fashioned into a thin plane sheet, is one of the most singular that can be witnessed in this or any other manufacture. The workman having collected on the end of his blowing tube, from the inside of the earthenware ring, as much glass in successive layers as experience teaches him is sufficient for one sheet or table (which should weigh about nine pounds)* rolls it into a pear-shape on a cast-iron

* It is remarkable that the tables of crown-glass made by expe-

plate or marver, an attendant boy slightly distending the mass by blowing at the same time; and the workman again softens the glass by holding it before the open mouth of a small furnace called the blowing furnace. He then rolls the bulb a second time on a marver, to correct any considerable inequalities in the thickness of its sides, and to elongate the neck by collecting a mass of glass on the end of the tube, thereby giving the bulb the form represented in fig. 8. The farther extremity of the bulb being supported on a horizontal smooth iron rod placed across a sort of stool (fig. 9), or what is more convenient, across a pit in front of the marver, the workman expands the bulb by blowing until it becomes

Fig. 9.

Fig. 8.



Fig. 10.

nearly spherical. After another softening and blowing at the blowing furnace it should be quite round, as fig. 10.

In this state the globe is taken to the "bottoming hole," which is a furnace similar to the flashing furnace, fig. 13, but having a much smaller opening,

rienced workmen seldom vary more than an ounce or two from the weight mentioned in the text.

where it is exposed to the action of flame, the workman being screened from the heat by a wall erected in front and a little on one side of the hole: the blowing tube is supported by a hook projecting from the wall. By revolving the globe while the part opposite to the tube is softened by the heat, the centrifugal force excited soon causes it to assume the form of fig. 11. When this is attained, the globe is withdrawn from the bottoming hole, and another workman applies a punto tipped with melted glass to the centre of the flattened part, while the first workman detaches the blowing pipe by touching the neck of the globe with a piece of iron wetted with cold water.

Fig. 11.

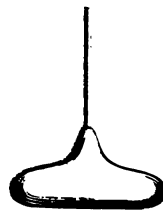


Fig. 12.



Fig. 13.

Holding the globe by the punto, the workman next exposes it to the action of a moderate flame before another circular opening called the "nose-hole," and by rotating it with a gradually increasing velocity expands the orifice produced through the removal of the former neck: by this the glass acquires the shape of fig. 12. It is next heated in a similar manner, but more powerfully, before the flashing furnace, fig. 13; and being rotated rapidly, it soon acquires the form shewn in fig. 14. On increasing the motion, the flattened globe at length flies com-



pletely open, being converted into a flat circular disc nearly sixty inches in diameter, of uniform



Fig. 14.

thickness throughout, except where it is attached to the punto.*

When the plate is sufficiently cool, the workman lays it flat upon a large iron fork held by an assistant, and cracks off the punto by applying a cold iron: the plate is then immediately transferred to the annealing arch (fig. 15), where it is placed,

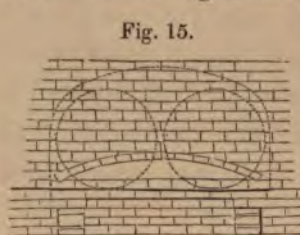


Fig. 15.

resting on its edge, in an iron frame, or on two poles of wood. The arch is generally made large enough to receive two rows of tables, as represented above by the dotted lines. The time re-

quired for the annealing is about twenty-four hours, according to the old plan, in which the whole arch is heated to nearly an uniform temperature and suffered to cool gradually; but a much shorter time suffices in the modern annealing process, where the arch is strongly heated at one end and nearly cold at the other, the tables being gradually drawn from the hot end to the cool end.

From each pot of glass, containing, when full, about half a ton of "metal," there are generally obtained one hundred tables; and at a moderate-sized establishment four such pots are worked off three days in each week throughout the year.

The scum which is removed from the surface of

* The knob in the centre of the disc, called the "bull's eye," is the part where the punto had been attached.

the melted glass, and the small residues in the pots, are "refined" by being poured into cold water. The glass thereby becomes disintegrated, so as to fall to a coarse powder, and a portion of the saline impurities present is dissolved out by the water. After being drained and dried, this glass is ready to be mixed and melted with fresh raw materials.

Broad-glass.—The materials from which the variety of glass known by the different names of broad window-glass, spread window-glass, inferior window-glass, German plate-glass, and British sheet-glass is made, are similar to those for making crown-glass. As commonly met with, spread-glass is coarser in texture and duller than crown-glass, and it always presents a wavy surface. In this country it was formerly made of very coarse materials, all the alkali being introduced in the form of a mixture of soap-boilers' waste and kelp; but this branch of the glass manufacture has undergone a considerable improvement of late, though the article now produced is considered to be inferior to crown-glass in lustre.

The processes for making this kind of glass and fashioning it into a thin plate are varied slightly in their details at different establishments, but the general nature of the operations is the same in all places. In one respect, the manipulations by which the plate is formed, differ essentially from the "flashing" process for crown-glass, as will presently be seen. The raw mixture is generally fritted with considerable agitation, for from twenty to thirty hours, and is introduced into the glass-pots while red-hot from the colcar. When the mass becomes per-

fectly vitrified and ready for working, which happens in about sixteen or twenty hours from the time of charging the pots, the workman collects about four pounds of the glass on the end of his tube, and blows it, after two or three heatings at a blowing furnace, into an elongated ball (fig. 16) of ten or

Fig. 16.



Fig. 17.

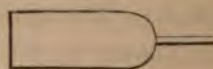
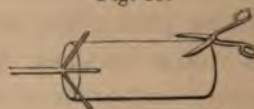


Fig. 18.



twelve inches in diameter, and nearly as long as the intended plate. The blowing pipe being steadily supported on a stool, an assistant makes a hole in the pear at the end exactly opposite the pipe, and the opening thus made is enlarged by a procello (see page 42), the glass being steadily turned round until the end of the pear is at length opened into a cylindrical mouth, as shewn in fig. 17. A three-pronged punto, tipped with melted glass, is then applied to the open mouth; and the cylinder being held perpendicularly, the blowing iron is cracked off in the usual way. The opening thus made, having been heated before one of the furnaces, is expanded by the procello until it becomes as large as the other end; when the cylinder is either slit through its whole length with a pair of shears (fig. 18), or cracked with a wet iron. The punto is then detached, and the split cylinder is introduced into a

sort of reverberatory furnace, called the "flattening kiln," the floor of which must be quite level and smooth, the cylinder being placed on its side horizontally with the slit uppermost. In this kiln the cylinder soon becomes softened by the heat, and the workman then opens it with the assistance of an iron instrument, until the whole lies upon the hearth as a flat sheet. From the flattening kiln the glass is transferred to the annealing kiln, the temperature of which is higher at one end than the other. The glass is first laid flat upon the hearth at the hottest part; then on a place called the "cooling bed," where it remains until it becomes quite stiff and rigid; and lastly, on one of its edges in another part of the kiln. When a sufficient quantity of the sheets has been thus piled away in compact masses, the whole is heated uniformly, and then allowed to cool gradually for several days, the entrance of external air being, at first, carefully excluded.

Some inconveniences are experienced in the working out of this process in the usual manner (as just described), particularly in the flattening and annealing; for obviating which, a patent has been lately granted to Mr. James T. Chance of Birmingham (1842). Instead of transferring the glass abruptly from the flattening kiln to the annealing kiln, and of lifting it from its first position in the latter to the "cooling bed" while the glass is still soft, and therefore liable to distortion, which has generally been done in order to save time, Mr. Chance adopts a plan of flattening and cooling, by which the glass, after having left the flattening chamber, is made to pass through a succession of decreasing temperatures;

not being lifted until it is quite stiff and rigid. In this plan, also, the workman is enabled to go on with the operation of flattening while the plates are being annealed; which is impracticable in the usual mode of procedure, because the temperature of the flattening kiln must be reduced with that of the annealing kiln, to which it is contiguous, and a waste of fuel and considerable expense for repairs are also experienced by the successive heating and cooling of the kilns.

In one of the arrangements described by the patentee, the flattening and annealing kilns are two circular buildings, communicating one with the other; each composed of an external wall and an internal masonry work, the intervening space being a circular arched vault. In each of these vaults is placed a cast-iron frame, supported on castors, and capable of being turned round at pleasure, by a connection with a winch fixed outside. The frame in the flattening kiln supports a series of "flattening stones," and that in the annealing kiln a number of metallic wires, radiating towards the centre of the building, for the purpose of supporting the plates to be annealed.

The glass cylinder is introduced into the flattening kiln through an opening in the external wall at about 80° from the middle of the communication between the two kilns, and placed on one of the flattening stones; it is then moved (by turning the winch of the cast-iron frame) until it comes abreast of another opening called the "working hole," which is about 135° from the middle of the communication between the two kilns; and immediately on the

farther side of the working hole is situated the principal furnace for heating the vault. Another smaller furnace for heating the flattening stones, previous to their receiving the cylinders, is placed on the opposite side of the hole through which the cylinders are introduced. After having been flattened by the workman in the ordinary manner, through the working hole, the glass is moved slowly around the vault (other cylinders being treated in like manner all the time) until it comes abreast of the annealing kiln. It is then placed, by means of an instrument introduced through a hole in the external wall, on the revolving frame in the annealing vault, and constantly moved through a gradually decreasing temperature, until it arrives at the coolest part, when it is withdrawn fully annealed. The stove for heating the annealing vault is situated a little on one side of the junction of the two kilns. Partitions are placed in the flattening and annealing vaults at certain intervals, to prevent the too rapid dissipation of heat from those parts where it is most required, and also to retard the entrance of cold air through the openings in the external wall. The openings left at the bottoms of the partitions are only sufficient to allow the frame with the stones and glass, or wires and glass, to pass underneath.*

* The claims of the patentee are the following. 1°. For methods of constructing and arranging flattening kilns, so that each sheet of glass may, without being lifted, be conveyed through a succession of temperatures, between the high temperature of the flattening chamber, and the temperature suitable for rendering such glass stiff and rigid, and in such manner that the workman may go on flattening several cylinders in the same furnace during the interval occupied in conveying each sheet of glass through each succession of temperature. 2°. The

3. BOTTLE-GLASS.

Until a few years ago, the laws of this country prohibited the use of any but the coarsest materials for making common bottles, in consideration of the duty levied on that glass being one-eighth lower than that on flint-glass. Almost the only alkaline material employed was soap-boilers' waste, and for the siliceous ingredient the commonest kind of river or sea sand was used. Not being restricted in this manner at the present time, the manufacturer selects such materials as may happen to be most available at the time, without having much regard to their purity. The composition of bottle-glass is therefore as little uniform as that of any other variety of glass; it being varied not only in different establishments, but in the same establishment at different times. The basis of this description of glass, however, is always a triple silicate of soda, alumina, and lime (at least in this country); the place of a portion of the lime being generally occupied by some magnesia and protoxide of iron, and that of a part of the alumina by peroxide of iron. The alumina is introduced in the form of clay.

The raw materials for making bottle-glass are commonly treated in much the same manner as for

2°. The combination of such an annealing kiln with a flattening kiln, that the sheets, plates, or panes of glass will not remain stationary during the annealing process.

And 3°, an apparatus for conveying sheets of glass along an annealing kiln, combined with a flattening kiln, by which the sheets of glass may be kept isolated, thereby shortening the time required for the process of annealing.

making broad-glass ; being generally fritted, before they are introduced into the glass-pots, in arches attached to the principal furnace. As the mixture always contains a very small relative proportion of the alkaline ingredient, its vitrification requires a very high temperature ; but it is generally complete in eighteen or twenty hours, and after the undissolved matter has subsided, the sandiver been skimmed off, and the glass become cooled down to the blowing consistency, the mass may be worked up into bottles.

To form a wine-bottle, a sufficient quantity of the melted glass is collected in a pear-shaped ball on the end of the blowing iron, and the ball is then introduced into an open cast-iron or brass mould, the tube being held vertically. The blower immediately closes the mould by pressing a pedal-lever with his foot, and blows the glass into the form of the mould. By withdrawing his foot from the lever, the blower opens the mould and then lifts up the bottle, which is immediately detached from the tube by applying a cold iron to the neck or mouth-ring. The bottle is lastly annealed in the ordinary manner.

The earth resulting from the disintegration of basaltic rocks, which may be obtained in the valleys of all basaltic countries, has been successfully used in the manufacture of bottle-glass ; but is now entirely abandoned, I believe, from the difficulty of procuring the earth of anything approaching uniform composition. It generally contains three or four per cent. of soda, about half its weight of silicic acid, and one-fifth its weight of oxide of iron ; the remainder consists of lime and alumina. A mixture of equal

weights of sand and basaltic earth was found by M. Ducros to produce a transparent glass of an olive-green colour. M. Alliot recommends, for the manufacture of bottles, a mixture of basaltic earth, sand, and refuse soda in equal parts, which affords a transparent glass of a greenish-yellow colour, smooth and lustrous.

The glass produced from the basaltic earth is specifically lighter than any common green bottle-glass, and is sufficiently hard and tough to sustain blows which would certainly break ordinary glass. If the earth is employed in considerable proportion, the colour of the glass is dark olive-green, or from that to a very deep yellow, which does not seem to be susceptible of correction by oxide of manganese. From its small relative proportion of alkali, the glass thus formed is enabled to resist the destructive action of corrosive liquids more effectually than most other kinds of glass; and might therefore, in all probability, be advantageously employed in the manufacture of carbuys, &c., for containing acids.*

4. PLATE-GLASS.

The materials from which plate-glass is made are of the same description as those for making English crown-glass, the only essential bases in combination with silicic acid being soda and lime; but the alkaline

* For an account of some experiments by M. Alliot on the fusion of basaltic earth, with a view to its application in the glass manufacture, see the treatise on the Manufacture of Porcelain and Glass in Lardner's Cyclopædia, page 192.

ingredient is introduced in much larger proportion in plate-glass than in crown-glass, hence the fabrication of the former does not require so high a heat as that of the latter. Great judgment is required in selecting the materials of the highest degree of purity consistent with economy. Until within a few years, all the alkali employed in the extensive cast plate-glass works at Ravenhead, near St. Helen's in Lancashire, was prepared by the decomposition of common salt and pearlash, as before described (page 27); the best soda crystals obtained by the common soda process from sulphate of soda not being sufficiently pure, when the usual mode of founding is adhered to. Soda crystals prepared in this way have long been employed, however, at the plate-glass works of St. Gobin in France (the first crop of crystals only being used); and of late, soda-ash of first-rate quality has been the only alkali employed by several English manufacturers of plate-glass.

Potash is never used in the plate-glass manufacture, except a small quantity which is occasionally introduced at some works in the form of nitre, for the purpose of destroying combustible matters. Glass made with soda and lime flows more freely than that made in a similar manner with potash and lime at the same degree of heat, and is consequently more suitable for casting. The circumstance of the volatility of sulphate of soda and chloride of sodium, which form the glass-gall in this instance, being greater than that of sulphate of potash and chloride of potassium, constitutes another important superiority of soda over potash.

In some works the lime is introduced in the state of chalk; in others, at Ravenhead for instance, as quick-lime; and in others as dry slaked lime. The sand as well as the lime and alkali should be scrupulously free from oxide of iron. All the materials, with the exception of the cullet or broken plate-glass, must be reduced to a state of fine division by sifting, having been previously ground if necessary. The sand employed in the works at Ravenhead is procured from the neighbourhood.

The proportions of the various ingredients employed for making plate-glass at St. Gobin are stated to be the following:

	ewt.	lbs.
Sand	7	0
Quick-lime	1	0
Dry carbonate of soda	2	37
Cullet, about	7	0
Black oxide of manganese, from	3 to 4	

The following proportions are recommended by Mr. Parkes :

Lynn sand washed and dried, 720 pounds; alkaline salt, containing 40 per cent. of soda, 450 pounds; quick-lime, slaked and sifted, 80 pounds; nitre, 25 pounds; and plate-glass cullet, 425 pounds. At present, the raw materials are introduced into the melting-pots without any previous fritting, both at Ravenhead and St. Gobin.

The room at Ravenhead in which the operations of founding and casting are conducted, called the "hall" or "foundry," is probably the largest under one roof in Great Britain, being 335 feet in length, by 155 feet in width.* The furnaces for the melt-

* The *halle* at St. Gobin is 174 feet by 120.

ing-pots, and for the pots called the "squares" or "cuvettes" (the use of which will be described presently), are placed in a range along the middle of the room lengthways, and occupy about one-third of the area of the room. The principal furnace, containing the melting-pots, is in the middle of this line. It holds six pots, similar in shape to the pots of the crown-glass house (page 33), each being large enough to contain very nearly a ton of melted glass. The average duration of these pots is nine months. The furnaces for the squares are not so large as the furnace for the melting-pots; each contains eight or nine squares, which are cubical-shaped pots, the length of each of the sides of which is about twenty-two inches. The floors of the furnaces on which the squares stand are on a level with the hall, and the arrangement of the furnaces is such as to allow of the ready introduction and removal of each of the squares. The annealing arches, of which there are forty-four at Ravenhead, are arranged in two rows along the sides of the hall, the wall of the hall forming one end of the arches. The opening of the arch through which the hot plates are introduced is quite similar to the opening of the arch represented in fig. 15, page 54, and is on a level with the table on which the plate is cast. The floor of the arch is about six inches lower than the bottom of the opening, the descent being moderated by a short slope. Each arch is about twelve or thirteen feet wide and forty feet deep, being capable of containing four or five plates of the largest dimensions which are cast. The plates lie flat on the floor of the arch, and not

on their edge, as the discs of crown-glass; nor is one placed over the other.

The table on which the casting is performed is an immense mass of cast-iron,* the dimensions being no less than twelve feet in length, seven feet in breadth, and seven inches in thickness. It is supported in a wooden frame, and runs on castors for the purpose of facilitating its removal from one annealing arch to another. One end of the table is placed close against the opening of the arch, and immediately beyond the other end of the table is placed a strong iron puppet, on which the iron roller for spreading the glass is laid when not in use. This roller is as long as the table is wide, and is about fourteen inches in diameter, the thickness of the metal being about one inch. The hall at Ravenhead is furnished with two of these casting-tables, one on each side of the rows of furnaces.

Bearing in mind these general arrangements of the hall, we may next consider, briefly, the complete course of operations practised in the production of a plate.

The melting-pots being raised to a full red or even white heat, are filled, on the morning of each day, with the raw materials; a fresh quantity being added as that previously introduced becomes melted down. Early on the morning of the following day, the contents of the melting-pots are transferred by

* The material of the casting-table at Ravenhead was formerly copper, but the liability of a mass of that metal to crack on the sudden application of an intense heat renders it improper for this purpose; bronze metal has been used at St. Gobin, but cast-iron is decidedly superior to either.

ladles to the squares, the latter being in their proper places in their furnaces, at a white heat; and the melting-pots are immediately afterwards charged afresh with raw materials. The glass remains in the squares until early in the evening, when it is generally ready for the casting: during this time it becomes "refined," the air-bubbles introduced by the transvasion being disengaged, and the heavy infusible matters subsided to the bottom. For two or three hours before the time of casting, the glass in the squares is cooled down to the proper consistency by closing the passages through which the air enters the furnaces.

The founding or melting of the raw materials, and the refining, are conducted in much the same manner at St. Gobin as at Ravenhead. The whole time required for these processes is thirty-two hours, sixteen of which are occupied in the founding, and the remainder in the refining and cooling in the cuvettes. The glass is then ready to be cast.

Some hours before the casting is commenced, fires are lighted in the small furnaces attached to those annealing arches which are to be used,* so as to bring the anterior part of the soles to a dull red heat. The casting-table being placed with one of its ends close to the mouth of the arch, and the glass in the squares being of the proper consistency for flowing easily and steadily, one of the squares is removed from the furnace on a low iron carriage furnished with two strong arms projecting in front of the wheels: two opposite sides of the squares have

* At Ravenhead, four arches are filled with plates daily, with the exception of Sundays.

a groove each, to admit the iron arms of the carriage. Being thus supported, the square is pushed over to one side of the casting-table, and is immediately raised by a crane a few feet from the ground, to allow of the removal of the scoria from the bottom and sides of the square, which might otherwise fall off on the table during the casting. The square is then lowered upon a plate of sheet-iron, and fixed between the two arms of a kind of tongs furnished with a handle at each end to enable the workmen to upset the square with facility. The scum on the surface of the glass having been removed by an iron instrument something like a sabre, and the metallic roller belonging to the casting-table being placed close to the mouth of the annealing arch, the square is raised by the crane until it is brought a few inches over the table and near the roller. A pendulous motion is then given to the square by two or three vibrations across the table, and its contents are poured out against the roller, proceeding gradually from one side of the table to the other, while the roller is at the same time steadily moved to the end of the table, and into the iron spring support placed there for its reception.

The thickness and breadth of the plate are determined by two metallic ridges, on which the roller runs, fixed one on each side of the table. The usual thickness of these ridges, and therefore of the rough

Fig. 19.



plate, is half an inch. To prevent the glass from flowing beyond the ridges, two iron instruments of the shape

shewn in fig. 19 are held by two men, one on each side of the table, close against the roller and the ridges. It seldom happens that sufficient glass is poured out to reach from one end of the table to the other; hence a ridge at the bottom of the table is unnecessary. While the liquid glass is flowing towards the bottom of the table, several of the workmen are busily occupied in scraping the surface of the table with instruments similar to a garden rake, but having a flat plate of steel instead of teeth.

As soon as the square has discharged its contents, it is replaced on the iron carriage and freed from the tongs; the greater part of the glass remaining on its bottom is then laded out into another square, and the empty square is returned to its seat in the furnace.

While the glass plate on the table is still red-hot and soft, an inch or two of the end farthest from the annealing arch is turned over so as to make a curl or hook; and before the plate becomes quite rigid, it is pushed into the arch. It is allowed to remain for a few minutes on the part of the floor of the arch nearest the mouth, which is at a dull red heat, and is afterwards gradually advanced towards the farther end of the arch to make room for other plates.

As soon as the last plate is introduced into the annealing arch, the mouth is closed with an iron door; and all the crevices, both around the mouth and the door of the furnace by the side of the arch, are carefully stopped up with wet clay. In this state the plates remain for three days, at the end of which period a little cold air is admitted by removing some of the luting around the mouth or door;

and after having remained in the arch for six days longer, the plates are in a fit state to be removed.*

The operations in the plate-glass manufacture which remain to be briefly adverted to are those of grinding, smoothing, polishing, and silvering.

* The following is an abstract from the specification of the patent for improvements in the glass manufacture, granted to Mr. Ragon in 1839. The claim of the method of casting plates, here described, to superiority, seems to be rather of a doubtful character. "Instead of passing a roller over the fused metal to force it into a flattened plate, I bring another flat plate or surface upon the melted glass, so as to compress it into a sheet, the thickness and dimensions of which are determined by strips or sides to the table, which prevent the upper plate descending too low down. Thus, by keeping the top plate pressing upon the surface of the glass until it has solidified, a much truer surface, or better plane, is obtained than by merely passing a roller over the glass, as is the common practice, and consequently much less grinding is required to get a true surface. But when the mass of fluid glass is too great to be controlled by the weight or pressure of the top plate or surface, in that case the latter is made to travel in grooves introduced in the side of the table, and should immediately follow, and simultaneously move, with the roller now in use; the object being always to confine or compress the glass until solidified, as above explained, and thus prevent the warping of the glass plates when exposed too promptly to the action of the atmosphere." (*Repertory of Patent Inventions*, vol. xiii. New Series.)

Besides the above process, and methods for preparing pure silicic acid, before alluded to (see note, page 26), the patentee claims, 1°, a mode of constructing the furnace for the melting-pots, by which the glass in the pots may be better protected from accidental impurities derived from the fuel, and the heat better regulated; 2°, a mode of heating the annealing arch by means of the waste heat of the furnace for the melting-pots; and 3°, the application of the vitreous slags of smelting furnaces to architectural purposes, by casting them in moulds into the required shapes. The pots for melting the glass are not situated in the fire-place, or rather in that part of the fire-place which contains the fuel, but in a chamber alongside, an upright series of bars being placed between to prevent the fuel from falling into the chamber. The flame passes between these bars, and escapes from the chamber at the opposite end into the annealing arch. The draught of the furnace is maintained by sending a blast of air through the ash-pit, and access to the pots is obtained by openings through the wall forming one of the sides of the chamber.

Before the rough plate is ground, it is squared at the edges and cut up into smaller plates by means of a glazier's diamond; all imperfections being examined minutely with a view of determining the most advantageous mode of dividing.

The materials with which the glass is successively rubbed, at Ravenhead, in the processes of grinding, smoothing, and polishing, are the following :

Grinding	{	1. Sand.
		2. Coarse emery (No. 1).
		3. Finer do. (No. 2).
		4. Finer do. (No. 3).
Smoothing ...	{	5. Finer emery (No. 4).
		6. Finer do. (No. 5).
		7. Finer do. (No. 6).
		8. Finer do. (No. 7).
		9. Finest do. (No. 8).
Polishing ...		10. Colcothar.

In the grinding of plate-glass the materials above mentioned are introduced successively between two plates; one of which, the lower, is cemented by stucco to a stone table at about two feet above the ground and perfectly horizontal; while the other is cemented to a frame to which a peculiar excentric motion is communicated by steam power. When the upper plate, which is about one-third the size of the lower, is in motion, the workman occasionally sprinkles a little of the grinding materials and water between the two surfaces, whereby each of the two plates may be ground to almost any required thinness. When each plate has been ground sufficiently on one side, both are reversed and ground in a similar manner on their other sides. Frequently several small plates

of the same thickness are cemented together to one table and ground at the same time. By the process of grinding the thickness of the plates generally becomes reduced to about one-half of the original thickness.

From the grinding room the glass plates, which are now perfectly level, are removed to the smoothing room, the operations executed in which are conducted, at Ravenhead, by females. The fine emery used in this process is introduced, as before, between two plates; the lower being fixed to a table, and the upper moved about by the hand.

After having been thus rubbed on both sides with wet emery powder of five degrees of fineness, the plates are transferred to the polishing room, where they are rubbed on each side with colcothar, which is oxide of iron, obtained by the calcination of green vitriol. The colcothar is spread on small rubbers of hat-felt, which are attached to frames kept in constant motion by steam power. This operation, which is continued for from twelve to twenty-four hours, completes the polishing, and the plates are then ready to be squared, if necessary, and be either sold in that state or silvered.

The process of silvering a plane mirror consists in the application to one side of the glass of a layer of tin-foil covered with mercury, which constitutes the reflecting surface. Both the instruments and the manipulations by which this is effected are extremely simple. Most of the operations are performed on a large stone table perfectly level and smooth, supported on an axis which runs through the middle, lengthways, so that it may be inclined a little at

pleasure by means of a screw fixed below. A gutter is placed around the edge of the table to collect the waste mercury, which falls through a pipe at one of the corners into a receiver below.

The operations consist, 1°, in the cleaning of the glass plate; 2°, in the preparation of the alloy of tin and mercury; and 3°, in the application of the alloy.

A piece of clean tin-foil, a little larger than the glass to be silvered, is placed upon the stone table, which, in this part of the process, must be perfectly horizontal; and the foil is scraped with a flat piece of wood covered with flannel to remove any wrinkles. A little clean mercury is then rubbed over the foil by a piece of flannel, so as to form an amalgam over the whole surface; after which, a sufficient quantity of mercury is poured on the foil to cover the latter all over to the depth of about one-eighth of an inch, and the surface of the mercury is scraped quite clean with a piece of flannel. The glass plate having been carefully rubbed on the side to be silvered, first with a damp cloth, and afterwards with a dry and warm cloth, a strip of flannel is laid upon one of the edges of the foil, and commencing at this edge, the plate is steadily pushed over the whole surface of the metal, so that neither air nor dust can remain under the plate. To expel the excess of mercury, a considerable pressure is applied to all parts of the plate by means of several leaden weights, and a slight inclination is given to the table to favour the drainage of the fluid metal. After having remained in this state for twenty-four hours, the weights are removed, and the superfluous edges of the foil

having been scraped off, the plate is removed from the table and placed for several days in a more inclined position, to complete the drainage of the mercury.

Plate-glass is not always fashioned, however, by casting. The process of *blowing* a plate of this kind of glass is very similar to the mode of blowing spread or broad glass, described at page 55; the minute differences observable in the manipulations in these processes being chiefly occasioned by the weight and bulk of the mass of glass operated on being considerably greater in the blowing of plate-glass than in the blowing of spread-glass. It is very difficult to blow a plate of glass of sufficient thickness for grinding to a level surface and polishing, of a size larger than fifty inches in length by forty inches in breadth. By the process of casting, plates of glass are produced of one hundred and sixty inches in length by eighty inches in breadth.

The flutings and triangular indentations which are sometimes seen on one side of plate-glass are produced by corresponding but reverse flutings and indentations on the surface of the heavy metallic roller with which the liquid glass is spread out upon the casting-table.

§ V. DEFECTS IN GLASS.

The attainment of a process for preparing *perfect* glass has for a long time, and with only doubtful success, engaged the attention of the experimental philosopher, as well as that of the glass manufacturer. The most important defects likely to exist in glass are *striæ* or wreath, knots, threads, and tears. *Striæ* are undulating appearances which result from a want of uniformity in the density of the mass. In consequence of this inequality, the rays of light passing through the glass become differently refracted and dispersed, thus producing a wavy appearance like what is perceived in looking through a liquid composed of two imperfectly mixed solutions of different strengths. This defect may exist to a considerable extent without being discernible by the naked eye, and consequently without being detrimental to the quality of the glass when applied to all ordinary purposes; but the smallest incongruity in the mass would render the glass quite inapplicable to the construction of optical instruments, where every distortion of the rays of light in their passage through the glass would be considerably magnified. Flint-glass is much more subject to this defect than any other kind of glass. The opaque knots which are sometimes perceived in glass may be either particles of earthy matter fallen from the furnace or abraded from the crucible, a portion of the glass-gall, or else imperfectly vitrified grains of sand. The appearances called threads and tears result from pieces of partially vitrified clay, which fell into the crucible

from the roof of the furnace, but did not mix uniformly with the glass. These semi-vitreous lumps or threads differ from the proper glass not only in colour, but in their degree of dilatation and contraction through change of temperature, which gives the glass a disposition to fly to pieces without any apparent cause. Another defect sometimes perceived in the less fusible varieties of glass is a want of clearness, owing to the presence of minute bubbles diffused throughout the substance of the glass. The presence of these bubbles indicates that the glass has not been maintained in a perfectly fluid state for a sufficient length of time to allow of their union and dispersion.

With the exception of the *striae*, these defects may be avoided without any extraordinary care and attention; and in the case of crown-glass, where the specific gravities of the materials do not greatly vary, and where the temperature at which the materials are vitrified is very intense, defects arising from the existence of *striae* are not of great importance. But in the case of flint-glass, the materials for which have a very unequal density, it is extremely difficult to obtain, by the usual process, a perfectly uniform piece large enough to form a disc of only a few inches in diameter; and the fitness of glass for being constructed into lenses depends much more on its uniformity in density or refractive power, than on its whiteness or brilliancy. If the raw materials have not been well incorporated, the pot of glass is very apt to contain an excess of oxide of lead in some parts and a deficiency in others, which pro-

duces a corresponding inequality in the density of the mass; and even in the slow refrigeration of a pot of pretty uniform glass, the heavier silicate of lead always subsides, and leaves the lighter alkaline silicate in excess at the upper parts; but if the mass is quickly cooled, it would be extremely brittle, and apt to fly to pieces on attempting to cut it.

The want of uniformity in a pot of flint-glass seems to proceed in a great measure from the unequal heating of the pot, the construction of the furnace being generally such as to allow the sides to be heated considerably higher than the bottom. When this is the case, the denser portions of glass, which subside to the bottom, remain there; but if the temperature of the inferior part of the pot is made considerably higher than that of the upper part, the denser glass would become expanded by the increased heat, and probably be diffused throughout the mass. The figure of a furnace said to be adapted to this object may be found in Dr. Ure's Dictionary of Arts, &c. art. Glass-making.

Another method of obtaining a pretty uniform pot of glass is by agitation, the glass being either poured by ladles from one crucible into another in the furnace, or else stirred by a rod of iron encased in stoneware,* as the naked iron itself would colour the glass. After being agitated, the glass must be allowed to stand quiet for a short time for the air-bubbles to be dissipated; and when perceived by the proof to be perfectly "fine" or free from bubbles, it should either be quickly cooled while in the cru-

* This mode of stirring was adopted by the late M. Guinand.

cible till nearly solid, or else be removed from the crucible in the liquid state, being gathered in successive layers on the end of an iron rod. If the glass is allowed to solidify in the crucible, the mass may be afterwards broken by a hammer into conchoidal lumps, to which a lenticular shape may be imparted by exposing them to a softening heat in a reverberatory furnace. The temperature of this furnace should be very equable, and not above dull redness. A method has been contrived for cleaving the mass of glass while cooling in the crucible, in such a manner that the fracture follows the direction of the more faulty parts; in which way masses of homogeneous glass weighing as much as forty pounds are said to have been obtained.

After several years spent in laborious experiments, the late M. Guinand, of Brennets, an inconsiderable village among the mountains of Neuchâtel in Switzerland, appears to have discovered some method of procedure, whereby homogeneous pieces of flint-glass, capable of forming lenses a foot in diameter, could be procured almost with certainty. An eminent French optician states that eight or nine out of ten object-glasses made of M. Guinand's flint-glass proved of excellent quality, but only one or two out of the same number made of glass from the English and French makers came up to the test. The process discovered by M. Guinand has not been made public, but the secret is said to be in the possession of his son and M. Bontemps, and the latter has made some important improvements on the process. A specimen of M. Guinand's flint-glass, of specific

gravity 3·616, has been analysed with the following results : silicic acid 44·3 ; oxide of lead 43·05 ; potash 11·75. These proportions nearly correspond with three equivalents of potash, five equivalents of oxide of lead, and eighteen equivalents of silicic acid. It is said that the freedom of the glass from bubbles depends, in a great measure, on the rigour observed in compounding the materials in the proper proportions, as well as from certain precautions in the management of the fire towards the end of the operation.

The results of a series of well-conducted experiments by Mr. Faraday, having for their object the discovery of a process for preparing homogeneous glass with some certainty, form the subject of the Bakerian Lecture in the Philosophical Transactions for 1830. The glass recommended by Mr. Faraday is a combination of silicate of lead with borate of lead, the materials being perfectly pure, and vitrified in a platinum crucible. If the air-bubbles are disengaged but slowly, it is advised to throw into the crucible a little spongy platinum, in fine powder, which should be stirred about with a platinum spatula. The powder readily subsides, and the glass may then be poured off quite clear and free from striæ. This glass is considered to be less attractive of moisture than most other kinds. From the limited scale on which this process would have to be performed, the suggestions of Mr. Faraday have not been carried out by manufacturers.

It may be observed, that an achromatic object-glass for a telescope or microscope, that is, an object-glass which does not afford coloured fringes around the

edge of the image, distinguished as *chromatic aberration*, must consist of two lenses made of different kinds of glass, differing in the proportion which their refractive power bears to their dispersive power. Flint-glass and crown-glass are well adapted for being formed into such a compound lens, the dispersive power of the former being nearly double that of the latter, while the mean refractive powers of the two kinds are nearly the same.

§ VI. COLOURING OF GLASS.

When certain metallic oxides are mixed with glass in a fluid or semi-fluid state, an intimate combination takes place between the glass and the metallic oxide, with the production of coloured compounds, which become dissolved and retained in the mass of glass without rendering it opaque. All the varieties of glass, and indeed, most saline bodies which possess a vitreous character, as borax and biphosphate of soda, are susceptible of being coloured in this manner by metallic oxides, but in many cases particular oxides are found to produce the richest colours with a particular kind of glass. Most of the colouring oxides afford more brilliant tints with the clear and white glass made of potash and lime, than with glass containing oxide of lead; but in a few cases, lead glass is decidedly preferable to potash and lime glass. The oxides which are mostly employed as vitrifiable colouring matters are the following: black and red oxides of copper, oxide of cobalt, oxide of iron, oxide of gold, oxide of man-

ganese, oxide of chromium, oxide of silver, oxide of platinum, oxide of uranium, and oxide of antimony.

These colouring matters are not always introduced into the glass in the form of oxides. Thus silver is sometimes applied as the chloride, and sometimes in the metallic state. But in whatever form the metal is applied, it seems to exist in the coloured glass as the oxide, in combination with silicic acid, probably as a double silicate, the other base being one of those proper to the glass. Certain metallic oxides which are decomposed by a comparatively slight elevation of temperature into oxygen gas and their metallic bases, resist decomposition at all attainable temperatures in contact with melted glass; and not only so, but the metal itself, if applied to the surface of the melted glass, becomes converted into an oxide by the acquisition of oxygen from the air. This is the case, for example, with silver.

The art of colouring glass is so comprehensive, in its details, that nothing more than a few general observations on the materials employed, and the ordinary modes of applying them, can be included in the present article. It appears to have been prosecuted at a period almost as early as that of the manufacture of glass itself. The earthenware beads with which some Egyptian mummies are adorned, are covered with a true glass coloured by means of a metallic oxide; and small pieces of transparent glass of a turquoise colour have lately been discovered among the tombs at Thebes, which are supposed to have been used as the glaze for beads.

Both the black oxide (protoxide), and the red

oxide (suboxide) of copper, are used as colouring materials for glass. The protoxide imparts either a bright blue or a full green, according to the manner in which it is applied. This colouring material is usually introduced in the form of oxide, obtained by heating pieces of sheet copper to redness with exposure to the air, and quenching them in cold water in order to detach the scales of oxide. A more convenient form is the subcarbonate, prepared by precipitation from a solution of the sulphate, with carbonate of soda. The acetate of copper is also sometimes used with advantage. To produce a full green glass the vitreous basis should contain some oxide of lead (though this is not essential to the production of the colour), and the oxide may be employed in any proportion between five and fifteen per cent. It is said that a beautiful blue glass may be obtained by means of the double subcarbonate of copper and ammonia, precipitated from the solution of the nitrate of copper by carbonate of ammonia. The black oxide of copper has been found to be the only colouring matter in some specimens of Egyptian blue glass, analysed by Sir H. Davy and M. Chaptal; but in other similar specimens, the oxide of copper is found to be accompanied by oxide of iron. The suboxide of copper tinges glass of a beautiful ruby-red, instead of a green or blue, but that colouring matter is very difficult of application. The intensity of the colour is increased by the addition of peroxide of iron, which imparts, of itself, a red colour to glass, but not so deep and brilliant as that of the suboxide of copper. One process for preparing this ruby-glass consists in mixing cream of

tartar with the green glass containing the protoxide of copper, in a melted state, whereby the protoxide becomes reduced to the state of suboxide; the glass swells up considerably on the addition of the cream of tartar, from the disengagement of gas, at the same time losing its green colour and becoming red, and when subsided, is fit for use. The colour of some specimens of ancient ruby-glass is due to the presence of suboxide of copper.

Several different colours may be communicated to glass by means of the protoxide and peroxide of iron. The protoxide, alone, gives a dull green colour, which may be made so deep as to appear black; while the peroxide affords a variety of shades from yellow to dark red. The green colour of the common bottle-glass is due, chiefly, to the presence of protoxide of iron, introduced as an impurity in the materials.* If the yellow or red glass containing peroxide of iron is exposed for some time to a very intense heat, the peroxide becomes reduced to the state of protoxide, and this glass consequently presents a green colour when cold; but by paying particular attention to the temperature of the melted glass, the decomposition of the peroxide may be prevented, and the yellow or red colour preserved. An imitation of the yellow topaz may be made by adding about one part of peroxide of iron to one hundred parts of the vitreous paste for artificial gems made according to one of the methods described at page 45. For producing a dark red, the oxide of iron may form as

* Mention has already been made of the use of the black oxide of manganese in reducing the colour which arises from the presence of protoxide of iron, by converting the latter into the peroxide (see page 30).

much as one-fourth or one-third of the mixture. The addition of alumina to the peroxide of iron is said to render the colour of the glass much clearer and less liable to alteration in the fire; the mixture of oxide of iron and alumina which results from the calcination of three parts of alum and one of copperas, affords a flesh-coloured combination with eight or ten parts of colourless glass. Peroxide of iron is more frequently used in mixture with other colouring metallic oxides, than alone.

Oxide of cobalt is the principal vitrifiable colouring material employed for the production of blue glass. No other metallic oxide possesses so intense a colouring power as this, one part being sufficient to afford a deep blue with one thousand parts of glass; and if the oxide is applied in a little larger proportion, the colour becomes so deep as to appear black. All kinds of glass may be coloured blue by this oxide with equal facility, and the colour is not in the smallest degree deteriorated by exposure to the highest temperature of a wind-furnace. The presence of oxide of cobalt has not been detected in any specimens of ancient blue glass.

This metallic oxide is also used in combination with other colouring oxides, with a view of producing a compound colour. Thus, various shades of green may be produced by mixing it with oxide of lead or oxide of antimony, and a violet by combining it with oxide of gold and oxide of manganese. A very fine black is imparted to glass by a mixture of oxide of cobalt, oxide of iron, and oxide of manganese. The pigment, *smalt-blue*, is a pounded potash-glass coloured with oxide of cobalt.

A very beautiful and delicate grass-green colour may be imparted to glass by means of oxide of chromium, which is the natural colouring matter of the green emerald. This colour is almost as fixed at a high temperature as the blue from oxide of cobalt. Oxide of chromium is the only green colouring matter employed by some experienced enamel-painters. Chromic acid tinges glass of a red instead of a green colour.

Oxide of manganese is extensively employed for imparting to glass a great variety of shades, from a delicate amethyst to deep violet or even black. One part of the oxide is sufficient to produce a fine amethyst colour with two or three hundred parts of glass. The colour supports a very intense heat without deterioration in the absence of any deoxidizing agent. (See page 30.) The amethyst may be imitated by a mixture of 5000 parts of a vitreous basis (as one of the pastes described at page 45), 20 parts of oxide of manganese, and 1 part of oxide of cobalt.

Some preparations of gold have long been employed to communicate to glass a superb purplish-red colour, nearly equalling that of the ruby, which it closely resembles. In preparing glass of this colour great attention and care are required to prevent the reduction of the oxide of gold to the metallic state, in which form gold communicates a dingy brown colour instead of a purple or red. The best preparation of gold for affording a red colour is said to be the compound of oxide of gold and peroxide of tin, called purple of Cassius, which is precipitated on adding protochloride of tin to a dilute solution of gold. One part of this powder is sufficient to

produce a good colour with eight hundred or a thousand parts of the vitreous base. When a very full ruby colour is required, it is usual to introduce a little pure oxide of antimony, the yellow tinge imparted by which is considered to improve the colour of the oxide of gold materially. It is remarkable that glass receives no colour from oxide of gold, unless the oxide of another metal proper is present, as oxide of lead, oxide of antimony, oxide of zinc, or oxide of bismuth. This glass acquires its colour, for the most part, while cooling; it being nearly colourless when in the melted state. Oxide of gold is much used at present as the colouring matter for ruby and rose-coloured toilet-bottles, &c.

Oxide of silver was at one time extensively used for communicating an excellent yellow colour to glass, being introduced as sulphate, as chloride, in the metallic state, and also in the form of the pure oxide; but this colouring matter is very little employed at present, it being superseded by others more easily applied and less expensive. The oxide of silver was frequently combined with the oxides of lead and antimony; each of which, by itself, tinges glass of a yellow colour.

The colouring matter in the delicate lemon-yellow glass vessels which have become so common within the last few years, is the peroxide of uranium. The colour of this glass is not affected by exposure to a very high temperature, and no particular precautions need be observed in conducting the firing. A greenish tinge may be given by introducing a very small proportion of carbonate of copper.

Chrome-yellow (chromate of lead) has also been

applied to glass as a yellow colouring matter with good effect.

A very excellent black glass may be obtained by adding to the vitreous basis some preparation of platinum containing, or capable of affording, the protoxide of that metal. On adding a solution of the nitrate of the black oxide of mercury to a solution of bichloride of platinum, a brown basic salt is precipitated; which, when washed, dried, and gently calcined, is decomposed into subchloride of mercury, which volatilizes, and protoxide of platinum, which remains behind, in a form well fitted for this application.

The substances employed for rendering colourless and some coloured glasses more or less opaque, like enamel, are phosphate of lime, fluor spar, arsenious acid, peroxide of tin, phosphate of lead, and phosphate of antimony. Phosphate of lime, which is the only one of these materials commonly employed at present, with the exception of fluor spar, is introduced in the form of finely powdered calcined bones, to the amount of from one-twentieth to one-thirtieth of the weight of the glass. A very beautiful opaline crystal may be obtained in this way. Peroxide of tin and arsenious acid were formerly much used for preparing opalescent glasses, but several inconveniences attend the use of these bodies which are not experienced with phosphate of lime. Opaque or translucent coloured glasses may also be obtained by combining bone-ash with the colouring oxide.

To colour glass uniformly, throughout its whole

substance, it is essential that the colouring oxide be intimately mixed with the glass, and both be brought into a state of complete fusion. But glass vessels and panes for windows are coloured, very commonly, merely on their surface, the body being an ordinary colourless glass. In stained and painted glass, the metallic oxides, mixed with vitreous bodies capable of being easily fused, and with certain fluid vehicles (very frequently oil of turpentine), are applied to the surface of the pane, commonly where a design is required, by means of a brush; but the pigments may also be applied from an engraved metallic plate or wooden block,* with gentle pressure, and the pane is then exposed in an oven or muffle to a temperature sufficient to fuse the vitreous flux and dissolve the colouring matter. The glass used for this purpose should be clear, colourless, and very difficult of fusion; hence crown-glass containing a small proportion of alkali is preferred.† In another method of obtaining a sheet of glass coloured on one of its surfaces, the glass-blower first collects the proper quantity of colourless glass on the end of

* Boiled oil is said to be the proper vehicle for vitrifiable pigments when *printed* on the glass. This application of boiled fixed oils, and also the use of an engraved metallic plate, as a printing surface, have been patented.

† Fluor spar (fluoride of calcium) is often applied to crown-glass in this way to produce a degree of opacity, without colour, in imitation of ground glass. The mineral is applied to the surface of a pane, in a state of most minute division, and mixed with a fluid vehicle. After the glass has been moderately heated, so as to dry the coating of fluor spar but not to fuse it, portions of the coating may be scraped off with a view of obtaining a transparent design on a translucent ground. On exposing the glass thus prepared to a high temperature in an oven, fluosilicate of lime is formed, which fuses into the substance of the glass to a small depth, thereby communicating a permanent opacity.

the blowing-iron, then dips this lump for a moment into a pot of melted coloured glass, and blows out the two together into a cylinder or globe, which is extended into a flat plate in the ordinary manner. This method has long been practised in Bohemia, and is now become very general for colouring crown-glass red by means of the suboxide of copper. Ornamental vessels of flint-glass are also coloured on their outside in a similar manner, and colourless facets may be produced on such vessels by cutting through the layer of coloured glass into the substratum of colourless glass.

A patent has been recently obtained for a method of ornamenting glass, as well as earthenware and porcelain, by a process similar to that for painting or staining glass. The glass vessel or plate to be coloured is first of all covered with a thin layer of some adhesive matter, for which purpose essence of lavender is said to be preferred by the patentee; and on this coating, the colouring oxides, in a state of very fine powder, and mixed with proper fluxes, are carefully dusted. The colour is then permanently fixed by the usual process of "firing." To obtain a coloured design, the surface of the glass may be printed with the adhesive varnish by an engraved block; and the superfluous colouring oxide which does not adhere to the varnish may be removed, previous to firing, by means of a pair of bellows. Or else, the glass may be entirely covered with the varnish, and the powder be sprinkled through a perforated screen, or an open fabric, such as lace, applied to the surface of the vessel or pane.

Articles made of flint-glass are sometimes orna-

mented with delicate white Argentine incrustations formed of dry porcelain clay, cemented into a solid by means of a little plaster of Paris. These figures being thoroughly dried are placed on the red-hot bulb of flint-glass, and are immediately covered with a thin layer of glass in a very liquid state, so as to completely enclose the incrustations. The polished external layer of glass gives the white figures a very agreeable silvery appearance, and they may be easily coloured, if required, by proper metallic oxides before being applied to the glass. Flint-glass vessels with coloured enamel figures on their external surface are sometimes prepared by placing the enamel figure in its proper place in the mould into which the glass is blown. The glass being very hot, the enamel figure becomes firmly cemented to the surface.*

Etching on glass.—The art of etching on glass by means of hydrofluoric acid may be practised on

* A very singular method of forming pictures of coloured glasses was practised by the ancients, which seems to have consisted in laying together fibres of glass of various colours, so adapted to each other that a section across the fibres afforded a representation of the object to be painted, and then cementing the bundle into a homogeneous mass. The following interesting account of two of these productions is given by Winkelmann in his "Annotations on the History of the Arts among the Ancients." "Each of them is not quite one inch long and one third of an inch broad. One plate exhibits, on a dark ground of variegated colours, a bird, representing a duck of various very lively colours, more suitable to the Chinese arbitrary taste, than adapted to shew the true tints of nature. The outlines are well decided and sharp; the colours beautiful and pure, and have a very striking and brilliant effect, because the artist, according to the nature of the parts, has in some employed an opaque, and in others a transparent glass. The most delicate pencil of the miniature painter could not have traced more accurately and distinctly either the circle of the pupil of the eye, or the apparently scaly

all kinds of glass, but the most proper description is good crown-glass. The facts on which this art is founded are, that glass becomes powerfully corroded by exposure to hydrofluoric acid, and that certain parts of the glass may be easily protected by a resist varnish, on which the acid exerts no action except at a high temperature. The varnish usually employed by artists for this purpose is either common turpentine varnish mixed with a little white lead, or a strong aqueous solution of isinglass. In

feathers on the breast and wings, behind the beginning of which this piece had been broken. But the admiration of the beholder is at the highest pitch when, by turning the glass, he sees the same bird on the reverse, without perceiving any difference in the smallest points; whence we could not but conclude that this picture is continued through the whole thickness of the specimen, and that if the glass were cut transversely, the same picture of the duck would be found repeated in the several slabs; a conclusion which was still further confirmed by the transparent places of some beautiful colours upon the eye and breast that were observed. The painting has on both sides a granular appearance, and seems to have been formed in the manner of mosaic works, of single pieces, but so accurately united, that a powerful magnifying glass was unable to discover any junctures. This circumstance and the continuation of the picture throughout the whole substance, rendered it extremely difficult to form any direct notion of the process or manner of forming such a work; and the conception of it might have long continued enigmatical, were it not that, in the section of the fracture mentioned, lines are observable, of the same colours which appear on the upper surface, that pervade the whole mass from one side to the other; whence it became a rational conclusion, that this kind of painting must have been executed by joining variously coloured filaments of glass, and subsequently fusing the same into one coherent body. The other specimen is of almost the same size, and made in the same manner. It exhibits ornamental drawings of white, green, and yellow colours, which are traced on a blue ground, and represent volutes, beads, and flowers, resting on pyramidally converging lines. All these are very distinct and separate, but so extremely small, that even a keen eye finds it difficult to perceive the subtle endings; those, in particular, in which the volutes terminate; notwithstanding which, these ornaments pass uninterruptedly through the whole thickness of the piece."

performing the process on a small scale, purified bees'-wax will be found to form a convenient varnish.

The piece of glass to be etched is first of all warmed in any convenient manner, and one of its surfaces is then rubbed over with the wax, the temperature of the glass being high enough to cause the wax to melt and be distributed uniformly over the entire surface. The glass is then set aside to cool; and when the wax is become quite solid, the design may be traced with a pointed, but not very fine, instrument, such as a bodkin. A carpenter's bradawl is a convenient tool for this operation, since, from being flattened at the end in one direction, it may be made to trace lines of different degrees of fineness, according to the position in which it is held. Care must be taken to cut through the entire thickness of the wax, so as to lay the glass quite bare through the whole length of the line.

The next part of the process consists in the application of the hydrofluoric acid. The vessel employed for this purpose is a shallow basin, either of lead or of Wedgwood's ware, (no glazed vessel should be employed,) large enough to include within its area every part of the design, when the prepared glass is placed upon its edge. The materials for generating hydrofluoric acid, consisting of one part of powdered fluor-spar, and about two parts of highly concentrated oil of vitriol, are introduced into the basin and well mixed; the glass plate is then laid on the edge of the basin with the waxed side undermost, and a moderate heat is applied to disengage the vapour of hydrofluoric acid. A spirit-lamp will be found a convenient source of heat, from the facility

it affords of increasing or decreasing the temperature at pleasure. Care must be taken to prevent the heat becoming high enough to melt the wax.

After being exposed to the acid fumes for a few minutes, the glass plate may be removed and cleaned. The lines where the wax had been removed are found to be covered with a white powder, which consists of silico-fluorides of the metallic bases of the glass. The greater part of the wax may be removed by scraping with a common table-knife, and the remainder by warming the glass before the fire and wiping it with tow and a little oil of turpentine. The design will then be found perfectly etched upon the surface of the glass, the depth of the lines being proportional to the time the glass was exposed to the acid vapour. Glass plates engraved in this manner are not adapted for printing upon paper, like a copper plate, from the facility with which they are broken by the pressure necessary to apply in printing.

In conducting this operation, care should be taken not to allow the hands to become exposed to the acid fumes, as the vitality of the parts would be instantly destroyed by the action of the acid. A dilute aqueous solution of hydrofluoric acid may be substituted for the vapour in the above process, with a similar result.

Glass grinding and cutting.—The implements employed in grinding and cutting glass are extremely simple, though necessarily very varied, owing to the great variety of work which has to be executed. The most important of the instruments employed in

this art are circular discs, seldom exceeding twelve inches in diameter, which are caused to work with great celerity on a horizontal axis, set in motion, in all large establishments, by steam or water power. Against the circumference of these revolving discs, the glass to be ground is held by the hands of the workman.

The thickness of the cutting discs and the forms of their edge are varied considerably; some being flat, others concave, others convex, and others wedge-shaped. Even forty or fifty discs with different-shaped edges may be found in the same workshop. Materials of very different degrees of hardness, from cork to wrought iron, are employed in the formation of these discs. Those made of wrought iron, which are very thin, are used to cut grooves in glass, by the aid of sand and water, which are caused to drop on the circumference of the disc from hoppers placed above. Cast-iron discs are also sometimes used in the roughest part of the operation, but the coarse work is usually done by a disc of fine sandstone wetted with water. When ground down to the proper shape, the glass is polished by exposure to softer discs, the action of which is generally assisted by various powders applied in a humid state to the circumference. Thus a copper disc is used with emery and oil; a disc of block-tin with peroxide of tin or tutty; a disc made of willow wood with fine pumice-stone, colcothar, or putty; and a cork disc having an edging of hat-felt, with putty or colcothar. For grinding down and polishing optical glasses, brass moulds of the required shape are employed, the grinding and polishing powders being,

1°, coarse emery; 2°, fine emery; 3°, fine pumice-stone, and 4°, finely washed colcothar, each being wetted with water. The polishing is sometimes completed by a mould of lead. The formation of optical glasses requires some dexterous and delicate manipulations, but the whole art of glass-grinding and cutting is too strictly mechanical to require any further observations on it in a work treating merely of the preparation and chemical history of this highly important and interesting article.



STARCH.

§ I. Properties and composition of Starch.—II. Preparation of Starch from Cereals.—III. Preparation of Starch from Rice.—IV. Preparation of Starch from Potatoes.—V. Arrow-root ; Sago ; Tapioca ; Salep ; Tous les mois, and Indian Corn Starch.—VI. Dextrin and Starch Sugar.

If a piece of dough made of wheaten flour and cold water is tied up in a linen bag and kneaded in cold water, a white pulverulent substance exudes, which is deposited on allowing the liquor to repose. When water no longer passes through the bag in a milky state, a dirty white or greyish substance remains in the bag, differing widely in properties from the separated powder, being characterized while moist by an extraordinary viscosity and adhesiveness. In this way the two essential constituents of flour are separated from each other: the viscid substance remaining in the bag is called *gluten*, and the white powder separated by washing is *starch*.

Starch is not a constituent of grains of wheat or the different cereals alone: with the exception of woody fibre or lignin, it is probably the most abundantly diffused of all proximate vegetable principles. It is contained in the seeds of all acotyledonous plants; in several round perennial roots which produce an annual stem; in tuberous roots, such as the potatoe; in the stems of many monocotyledonous

plants, especially of the palm tribe; in unripe apples and pears, according to M. Liebig; and lastly, in several lichens. It rarely occurs in the stems and branches of dicotyledonous plants. In whatever part of the plant starch exists, it is contained in the cavities of the cellular substance, not attached to the cell, but perfectly isolated and surrounded with an aqueous liquid.

Several varieties of starch are found in commerce presenting slight modifications in their physical characters, according to the plants from which they are derived, and the processes by which they are extracted. The various sorts have hence received particular designations. But chemically speaking, there is only one kind of starch, which is found to be possessed of the same chemical characters and the same composition, from whatever plant or part of the plant it is derived: so that the several varieties must not be viewed as distinct species, but as mere structural modifications of the same chemical substance.

The principal varieties of starch which have received applications either in the arts or in domestic economy, are the following:

Common starch, derived from the grains of cereals, especially of wheat.

Potatoe starch, derived from the tubers of the potatoe.

Arrow-root, derived mostly from the roots of the *maranta arundinacea*.

East Indian arrow-root, chiefly from the tubers of the *curcuma angustifolia*.

Sago, derived from the pith of palms of the genus *sagus*.

Cassava and tapioca, derived from the tuberous root of the *Jatropha manihot*.

Indian corn starch, derived from the *Zea mais*.

Salep, supposed to be derived from the roots of different species of *orchis*.

Tous les mois, supposed to be derived from *canna coccinea*, and

Rice starch.

§ I. PROPERTIES AND COMPOSITION OF STARCH.

In a state of purity, starch is a fine, white, tasteless, and inodorous powder. It gives a peculiar sound when squeezed between the fingers, and feels slightly crystalline, especially tous les mois and potatoe starch. It is insoluble in cold water, in alcohol, and in ether. In boiling water, starch resolves itself into a mucilaginous liquid which forms a jelly on cooling. Pure starch is soluble in dilute acids, and forms a transparent solution which undergoes a remarkable series of changes by ebullition. The recent solution is coloured deep blue by an aqueous solution of iodine, but after a short boiling iodine produces a purple colour, and on continuing the boiling iodine at last ceases to produce any colour. In this experiment the starch is converted first into a substance having the properties of gum, called *dextrin*, and afterwards into a variety of sugar, distinguished as starch sugar, or grape sugar.

Starch is soluble in strong solutions of the caustic alkalies. If brayed in a mortar with a concentrated solution of potash, starch unites with the alkali, forming a transparent gelatinous compound, which is pro-

bably of definite constitution, and not a mere mixture of starch and alkali. This compound is soluble in water and in alcohol, and starch is precipitated from such solutions by acids. When a solution of starch is mixed with lime-water, with a solution of caustic barytes, or with a solution of subacetate of lead, a precipitate is produced consisting of a definite combination of starch with the base applied. A solution of starch is also precipitated by an infusion of galls and by a solution of borax. When heated with moderately strong nitric acid, starch is oxidated and converted into oxalic acid, and at least one other acid, the nature of which has not been exactly determined. No mucic acid is produced, as happens when gum is heated in nitric acid.

Starch dried at the temperature of 212° has the following composition :

12 eq. of carbon	72	44.44
10 eq. of hydrogen	10	6.17
10 eq. of oxygen	80	49.39
1 eq. of starch	162	100.00

The composition of starch dried at common temperatures is $C_{12}H_{12}O_{12}$; by exposure to a temperature of 212° , it loses, therefore, two equivalents of water.*

* The compound of starch and oxide of lead was found by M. Payen to have the composition $C_{12}H_9O_9 + 2PbO$, which renders it probable that the composition of anhydrous starch is $C_{12}H_9O_9$: the hydrate obtained by drying at the ordinary temperature will then contain three equivalents of water; and that dried at the boiling point, one equivalent of water. We have then the following series :

Anhydrous starch	$C_{12}H_9O_9$
Starch dried at common temperatures	$C_{12}H_9O_9 + 3HO$
Starch dried at 212°	$C_{12}H_9O_9 + HO$
Compound of starch with oxide of lead	$C_{12}H_9O_9 + 2PbO$

Though possessing the chemical characters of a pure and distinct principle, starch, singularly enough, is possessed of an organized structure. When examined by the microscope, it presents the form of rounded grains, the size and shape of which differ not only in starch procured from different plants, but even in that from the same plant at different times, and from different parts of the same plant at the same time. Thus, the diameters of the granules of potatoe starch vary from the seven-thousandth of an inch to the two-hundredth of an inch. Fig. 20 is a

Fig. 20.



representation of the ordinary appearance of potatoe starch when viewed by the microscope with a power of two hundred diameters. The largest granules obtained from the seed of the millet (fig. 21, with the same magnifying power) do not exceed in diameter, according to Raspail, the four-hundredth part of a millimetre, that is, very nearly, the ten-thousandth of an inch. The granules of starch obtained from wheat (fig. 22), are more regular in form than those from the potatoe.

Fig. 21.




Fig. 22.



The size of the granules increases with the age of the vegetable, and in certain organs the shape also changes. In the month of June, starch extracted

from the tuberous root of the iris (*iris florentina*)

Fig. 23. presents the appearance of fig. 23, with
 a power of one hundred diameters; but
 on allowing the tubers to repose in a
 shaded place in the open air for fifteen days, the
 starch then appears of the irregular forms in fig. 24.

Fig. 24. In the tuber vegetating in the
 earth, the starch does not ac-
 quire this appearance before
 autumn (Raspail, *Chimie Organique*, t. i. p. 452,
 2^{me} ed.). The granules of starch in the seed of the
 pea are three or four times as large as those in the
 expressed juice of the stalks (Liebig).

Leeuwenhoeck had observed in 1716, by means
 of the microscope, that each granule of starch is
 composed of an envelope differing in its characters
 from the interior globule. This observation, after
 having been entirely forgotten, was revived in 1825
 by M. Raspail, who was led, by a series of experi-
 mental researches on the nature of amylaceous prin-
 ciples, to the following conclusions:

1°. The granule of starch is composed of an in-
 soluble tegument and a soluble gummy interior, which
 is the substance now known as dextrin (page 99).
 2°. The effect of a gentle heat on starch is first
 the expansion of the granule, and afterwards the
 bursting of the envelope; the rupture may occur in
 dry or wet starch. The application of many che-
 mical agents, such as sulphuric acid and hydrate
 of potash, is attended with the rupture of the en-
 velope merely on account of the heat produced by
 the combination of these bodies with the humidity
 of the atmosphere or of the starch. 3°. When starch

is boiled in a large quantity of water, the dextrin liberated through the rupture of the envelope dissolves, and the insoluble tegument remains for a time in suspension, but is at length deposited. The teguments have twenty times their original size, and form when in mass a tremulent opaque jelly. 4°. When the limpid solution decanted from the deposit of teguments is evaporated at a moderate heat, it affords a substance having the external characters of a gum; the solution of which is precipitated by alcohol, and infusion of galls, but it is not coagulable by heat. 5°. Iodine produces a blue colour both with the teguments and the soluble matter, but not with the latter after it has been evaporated to dryness. The teguments retain the property of being rendered blue by iodine when dry.

For some time these conclusions of M. Raspail obtained pretty general assent, but more recent investigations have shewn the inaccuracy of some of his positions. The ideas now generally entertained concerning the constitution of the starch granule are as follows:

Instead of being formed simply of a tegument and of a homogeneous interior, the granule is composed of concentric layers of unequal thickness; but both the interior and the exterior are essentially one and the same substance, the difference in appearance resulting from a different state of aggregation and of hydration. The interior of the granule as well as the exterior is insoluble in cold water, or, at least, its solubility is so small that one thousand parts of cold water are required to dissolve one part of starch. It is not, therefore, identical with gum or with

dextrin, which substances are easily dissolved by cold water; but it is capable of being converted into dextrin by the application of heat, a circumstance which appears to have been sometimes overlooked by M. Raspail.

When granules of starch are well rubbed in a mortar with some hard powder, such as sand, the envelope is broken and the interior becomes exposed. If the mixed powder is put into cold water, the starch soon swells up into a tremulent jelly, but does not dissolve to a greater extent than above mentioned. A similar change takes place when the uninjured grains are thrown into water at the temperature of 140° Fahr. They imbibe water, swell, burst their envelopes, and form a jelly. But the jelly is not to be considered a solution of starch. It has imbibed water as a sponge, and if placed on bibulous paper it imparts to the latter its moisture, shrinks up and dries to a mass resembling horn, insoluble in cold water. The name *amidin* has been applied to this gelatinous starch.

Amidin is readily dissolved by boiling water, and if the mucilaginous solution which it affords is passed through a double paper filter, no granules or any solid matter can be perceived in the liquid by the microscope. If the solution is strong, it deposits much of the starch on cooling in a gelatinous state. M. Payen has made the curious observation, that when a solution of starch is frozen, that substance separates from the water and contracts into a kind of tissue which is not re-dissolved on the thawing of the ice. The tegumentary matter which remains undissolved at first, when starch is boiled in water, amounts to

about three or four parts in a thousand of starch, but this may also be dissolved by a prolonged ebullition.

When granules of some varieties of starch are examined by a high magnifying power, their surface appears to be marked with excentric rings surrounding a well-defined point. This appearance is exhibited in the annexed figure, which represents a granule of the starch known as *tous les mois*. The origin of these apparent wrinkles is not quite obvious. They are regarded by Raspail as indications of a spiral attached to the interior of the tegument, and proceeding from the point or hilum; but M. Fritzsche considers them to be evidences of the existence of the concentric layers already alluded to. The hilum is usually considered to be an aperture leading into the interior of the granule, by which the amylaceous matter forming the internal laminæ is introduced.

Fig. 25.

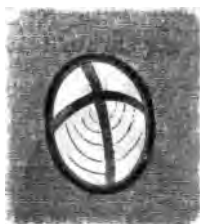


When swelled by moisture, granules of starch are possessed of double refraction, in consequence of the pressure exerted by the teguments upon their contents, and present a very beautiful appearance when viewed in a microscope by polarized light,* for which purpose they may be put up either in Canada balsam or water. When the planes of polarization of the polarizer and analyser are at right angles to each

* To obtain the polarized light, a Nicholl's prism or a tourmalin should be fitted beneath the stage on which the object is to be placed, so as to polarize the light reflected through the object by the mirror attached to the microscope. This is the "polarizer." Another Nicholl's prism or a tourmalin (the "analyser"), must be attached to the eye-piece of the microscope.

other, a distinct black cross is perceived (such as that exhibited in similar circumstances by doubly refracting crystals), the centre of which is at the

Fig. 26.



hilum of the granule, as represented in the annexed figure. The remainder of the granule is white, but the field or ground is black or grey. On rotating either the analyser or polarizer 90° , the black cross is replaced by a white one, the other parts of the granule becoming dark:

the field is then white.

If a thin plate of mica or selenite is placed anywhere between the eye and the reflector of the microscope, the edges of the cross and the intervening spaces become most beautifully coloured, and the field of view also assumes a tint dependent on the thickness of the mica or selenite. The adjoining spaces on either side of the cross exhibit complementary colours, which change on revolving the analysing plate, and become complementary at every quarter of a revolution. All the varieties of starch present this appearance, but not with equal distinctness, partly on account of their unequal state of distension. It is more evident in *tous les mois*, potatoe starch, and Indian corn starch, than in wheat starch, barley starch, and some other kinds.

If starch is dissolved in hot water, the solution allowed to cool and then filtered through paper, alcohol produces a precipitate in the solution which presents an evident spherical structure when examined with the microscope. The size of the granules is less than the ten-thousandth part of an inch.

We are indebted to M. Jacquelin for some very interesting observations on this subject (*Annales de Chimie et de Physique*, t. lxxiii. p. 167). When starch is heated with from five to fifteen parts of water under pressure in a Papin's digester to the temperature of 302° Fahr. (150° Cent.), for about two hours, everything is dissolved except the outer coating, and the solution, if near the boiling point, is sufficiently thin to be filtered through paper. As the liquid cools, it deposits a considerable quantity of starch in the form of white granules, opaque when in mass, and denser than water, subsiding from that liquid almost as quickly as potatoe starch. When dry, this deposit is white, but it wants the lustre of common starch. On examining these granules by a microscope with a power of two hundred diameters, M. Jacquelin observed them to be spherical, transparent and uniformly $\frac{1}{1000}$ of a millimetre ($\frac{1}{12500}$ of an inch) in diameter.

The most remarkable chemical change which the starch undergoes in this experiment is an increase in solubility in water. The granules are slightly soluble at 54° Fahr., but in a much larger proportion at 158°, and in larger still at the boiling point. At the freezing temperature, however, they are scarcely at all soluble. The granules are coloured blue, and not purple, by iodine; and a precipitate is produced in their aqueous solution by alcohol.

The composition of the granules is the same as that of starch dried at 212°, that is $C_{12}H_{10}O_{10}$; but M. Jacquelin always obtained about 0.25 per cent. of nitrogen from the granules, and a little larger amount from ordinary starch. He considers a small

quantity of nitrogen to be essential to the constitution of all the varieties of starch.

The peculiar appearance which starch presents when brought into contact with a solution of free iodine, already alluded to, constitutes a most delicate test for either starch or iodine. If an aqueous solution of iodine is applied to the ordinary granules of starch under the microscope, the colour of the granules may be observed to become first purple, afterwards violet, and at last, if the iodine is in excess, as when tincture of iodine is applied, deep blue; but the granules undergo no change in form or in size. If the coloured granule is brought into contact with a dilute solution of ammonia, with very dilute caustic potash or with lime-water, it parts with iodine and reassumes its original transparency without any change in form or dimensions.*

When a very dilute solution of starch, rendered blue by a small quantity of iodine, is heated, it loses

* A difference of opinion exists among chemists concerning the nature of this compound of iodine and starch. By some it is regarded as a mere mechanical mixture of the two substances, but others consider it to be a true definite compound of starch and iodine. From an analysis of this substance, by Lassaigne, it seems to be composed of two equivalents of iodine and one equivalent of starch. It is formed whenever free iodine is brought into contact with starch, and may be obtained in a state of purity by adding an alcoholic solution of iodine to a clear solution of starch containing some muriatic acid. The precipitated *iodide of starch* is collected on a filter and washed with small quantities of water until the filtered liquid exhibits a very blue colour; it may then be removed from the filter and dried *in vacuo*, being supported over a surface of oil of vitriol. It is then obtained as a brownish-black and brilliant gummy mass, easily pulverizable when dry, but it becomes viscous when exposed to the atmosphere through the absorption of moisture. It is insoluble in hydrochloric acid, but soluble in water, giving a deep blue solution.

all its colour at the temperature of 158° or 160° Fahr.; but if concentrated, a temperature of 194° is requisite to produce that effect. On the cooling of the liquid the blue colour reappears, unless the solution has been boiled; in the latter case the iodine appears to have combined with the elements of water, with formation of iodic and hydriodic acids. The blue colour may then be restored by the addition of a little hydrochloric or oxalic acid.*

§ II. PREPARATION OF STARCH FROM THE CEREALS.

Starch forms the principal constituent of the seeds of all the cereals. The other ingredients are gluten, gum, and sugar. The proportions in which these substances exist differ not only in various cereals, but also in different plants of the same kind, according to the soil, mode of culture, season, and climate. All the cereals are adapted for the manufacture of starch; but only wheat, barley, and rice are employed on the large scale.

The *gluten* with which starch is accompanied in these seeds is not a pure principle, but contains at least two, and probably three, distinct substances. As obtained by the process mentioned at the com-

* Chlorine and bromine also form compounds with starch, but that with chlorine is probably not of definite constitution. Dry starch absorbs chlorine gas and forms a liquid mass of a brown colour, containing much free hydrochloric acid. A little carbonic acid is evolved at the same time. The so-called *bromide of starch* is precipitated as an orange powder on mixing a solution of starch in water acidulated by muriatic acid, with an aqueous solution of bromine. This compound is decomposed by heat with great facility, bromine vapour being evolved. A slight exposure to a gentle heat destroys the colour of bromide of starch, but it reappears to a certain extent on cooling.

mencement of this article, gluten, when moist, is an exceedingly tenacious and elastic substance, capable of being extended into twenty times its original length. In a lump it is of a greyish colour; but when drawn out very thin it is whitish, and much resembles the animal tendon. The adhesiveness of paste made of wheaten flour is due to the presence of gluten, and this substance has been sometimes employed alone to cement broken pieces of porcelain. The sponginess of bread and the viscosity of dough are also owing to the adhesiveness of gluten; and the absence of this substance in potatoe flour renders the latter unfit, alone, for the preparation of bread. By a gradual exsiccation gluten becomes hard, brittle, translucent, and of a dark brown colour. It is soluble in acetic acid and in alkalies.

The *gum* contained in wheat is not quite identical with gum-arabic. The latter when treated with nitric acid gives rise to mucic acid, but the former produces oxalic acid and carbazotic acid, or the bitter principle of Welter. It seems to contain nitrogen as an essential constituent. As existing in the seeds, the *sugar* of wheat, &c., is probably identical with cane sugar, but it cannot be easily separated in a crystalline state.*

The material to which the starch manufacturer gives a decided preference as the source of starch,

* Analyses of the flour of eight varieties of common wheat by Vauquelin gave the following as the mean composition :

Water	10.3
Gluten	10.80
Starch	68.20
Sugar	5.61
Gum	4.11

Analyses

PREPARATION OF STARCH FROM THE CEREALS. 111

when the ordinary processes are made use of, is wheat. If damaged by exposure or long keeping,

Analyses of three varieties of wheat by M. Fuss afforded the following results :

Gluten	15.04	19.56	15.51
Starch	56.03	56.67	58.90
Vegetable albumen	0.15	0.88	0.30
Uncrystallizable sugar	0.60	0.60	0.68
Gum	0.41	0.48	0.40
Acid phosphates	0.08	0.06	0.06
Fibrin and bran	8.30	6.66	6.99
Water	9.39	8.45	9.70

The following table shews the proportions of starch and gluten per cent. contained in several varieties of wheat, &c., as determined by Sir H. Davy (Agricultural Chemistry), Vauquelin, and other chemists :

	<i>Starch. Gluten.</i>		
Middlesex wheat	76.50	19.00	Davy.
Spring wheat	70.00	24.00	"
Mildewed wheat of 1806	17.10	3.20	"
Blighted wheat of 1804	52.00	13.00	"
Thick-skinned Sicilian wheat of 1810	73.50	23.00	"
Wheat from Poland	75.00	20.00	"
North American wheat	73.00	22.50	"
Flour of French wheat	71.49	10.96	Vauquelin.
" of hard wheat of Odessa	56.50	14.55	"
" of soft wheat of Odessa	62.00	12.00	"
Wheat of French bakers	72.80	10.20	"
Flour of the Paris hospitals, (2nd quality) ...	71.20	10.30	"
" " (3rd quality) ...	67.78	9.02	"
" of triticum hybernum	68.00	24.00	Vogel.
" of triticum spelta	74.00	22.00	"
Rye flour	61.07	9.48	Einhof.
" from Poland	60.80	9.40	Greiff.
White oatmeal	59.00	4.30	Vogel.
Barley meal, besides 55 of hordein	32.00	3.0	Proust.
Oats from Scotland	64.10	8.70	Davy.
Rye from Yorkshire	64.50	10.90	"
Common beans	42.60	10.30	"

Wheat affords very little ash on incineration ; scarcely more than fifteen parts in ten thousand. It consists chiefly of phosphates of soda, lime, and magnesia, with a trace of silica. It contains but a very feeble trace, if any, of sulphuric acid.

it is still available in this manufacture, starch being far less subject to decomposition than the other constituents of wheat.

The simplest method of separating starch from gluten, and the other substances with which it is accompanied in wheat, is by the mechanical process alluded to at the commencement of this article; that is, by washing dough, enclosed in a linen bag, in a gentle stream of cold water (page 97). But the starch thus obtained is not wholly free from gluten. The complete removal of the latter is effected by a very different process, consisting in the application of some liquid in which the gluten can dissolve, but in which the starch is insoluble. For this purpose there may be employed either .

1°. Dilute acetic acid, or

2°. A very dilute alkaline solution.

When a mixture of starch and gluten is digested in either of these liquids, the gluten dissolves and leaves the starch unacted on.

The employment of an alkali in the preparation of starch from the grains of cereals, or rather the application of an alkali on the large scale, is a recent and very important improvement in the manufacture. As it is practised more particularly in the preparation of starch from rice, we shall have occasion to recur to it under that head.

The principal solvent of gluten in the old processes is acetic acid. This acid is not applied immediately as the caustic alkali is, but is generated in the liquor in contact with the impure starch by exciting a fermentative decomposition of a portion of the gluten and likewise of the starch itself. That

starch may be separated from bruised wheat by the simple process of washing in water has been known for many ages, but in the common processes the separation is almost wholly effected by the action of acetic acid formed by fermentation. The method generally practised in this country in the present day is the following. The wheat, coarsely ground between iron rollers, is digested in a vat with sufficient water to wet it thoroughly. A fermentation commences in three, four, or five days, according to the state of the weather; the mixture soon settles, and is then transferred to a large fermenting vat with a quantity of water. After having remained here for a fortnight or three weeks, the deposit is removed to a stout basket, in which it is washed by a stream of water, being constantly stirred. The bran remains in the basket, and the milky liquor which comes through, containing the starch, is strained through a hair-sieve into a square tub called the *frame*. In about twenty-four hours the impure starch settles to the bottom; the supernatant liquor is then withdrawn by plugs at different heights in the sides. The deposit consists of two layers; a thin light mucilaginous sediment, called the *slimes*, on the top; and underneath, a white coherent layer of impure starch. The slimes being removed, fresh water is introduced, and the mixture after agitation is thrown on a finer sieve than that previously used. When the starch is deposited from the percolated liquid, the latter is decanted, and the remaining slimes being removed, the starch is again mixed with fresh water. After being once more passed through the sieve, the mixture is allowed to stand for several days, so that

the deposit of starch may become firm. It is then fit to be "boxed." The blue tint of starch is usually imparted by the addition of a little smalts at the last sieve. In a recent patent for some improvements in the starch manufacture, Mr. Berger claims the use of artificial ultramarine as a substitute for smalts in the tinting of starch. Any trace of acid which may be present in the starch must then be carefully neutralized by the application of an alkali.*

When the moist starch is sufficiently firm, it is shovelled into oblong wooden boxes, of from four to five feet long, one foot broad, and about six or seven inches deep, perforated at its bottom, and lined with a linen cloth or thin canvas. When the starch is become tolerably hard, it is taken out of the chests, cut into pieces of five or six inches square, and set to dry on half-burned bricks. By their porosity the bricks imbibe the moisture of the starch, without the under-surface of the latter becoming very hard. After having remained on the bricks for from eight to ten hours, the pieces are put into the *stove*, which is a square building, moderately heated from below, and fitted up with racks on every side. When tolerably dry, the pieces are taken out of the stove and removed to a table, where the sides, consisting of a slimy crust, are

* The presence of a minute quantity of an alkaline carbonate rather improves starch than otherwise, as it serves to neutralize the small quantity of acetic (and probably lactic) acid which is produced on starched goods through the fermentative decomposition of a portion of the starch. Starched cotton goods, when laid by for several months in a humid situation, invariably become weakened in the fibre, through the action of the acid thus generated.

carefully scraped off with a knife. The remainder, which is pure starch, is then packed up in the papers in which it is sold, and returned to the stove pretty strongly heated, where it remains until quite dry. During the desiccation, it splits with much regularity into the prismatic columns in which wheat starch is commonly met with.

During the fermentation of the grains in the process just described, a very offensive odour is developed, arising from the putrefactive decomposition of the azotised substances present. The liquor which remains after the fermentation is very foul and acid, and is hence called "sour water." It contains alcohol, acetate of ammonia, acetic and lactic acids, phosphate of lime, and gluten. The fermentation which takes place first is the vinous, at the expense of the sugar and a considerable portion of the starch: carbonic acid and alcohol are thus formed; the former is evolved as gas, and the latter remains in the liquor. But when exposed to the air and in presence of azotised matter in a state of decomposition, alcohol does not remain long without undergoing the acetous fermentation, and it is by the acetic acid thus formed that the complete separation of the starch and gluten is effected. The decomposition of a portion of the gluten gives rise to ammonia, which unites with some of the acetic acid to form acetate of ammonia. The lactic acid is a secondary product arising from the fermentative decomposition of a portion of the starch. It probably assists the acetic acid in dissolving the gluten.

The loss of a great portion of the starch, and of all the gluten, and the insalubrity of the volatile

products of the fermentation, render the improvement of this process highly desirable. The inconveniences have been overcome, however, by partially reverting to the old method of making starch; that is, by simply washing dough in water. The vessel in which the dough is washed is a kind of trough furnished with a double bottom; the uppermost contains numerous small perforations. The dough, which is made with a very small quantity of water, is stirred about in the trough with a large pestle, water being at the same time poured in gently at the top. A wooden box is placed below the trough to receive the water which passes through the dough. It is said that nearly the whole of the starch may be thus separated from the gluten, the latter remaining in the trough as a homogeneous tenacious mass.

The deposit of starch obtained from the milky washings is contaminated, however, with appreciable quantities of gluten, and other impurities derived from the flour. To separate these, the supernatant liquor is decanted, and replaced by a quantity of fresh water: the mixture is well agitated, and allowed to stand in a large tub for one or two days, during which it undergoes a slight fermentation. The fermented liquor is decanted, and after another washing, the starch may be dried, as in the ordinary process.

By this process there are obtained about 55 per cent. of starch, and about 30 per cent. of gluten; while the common process by fermentation affords only 45 per cent. of starch, and no gluten.*

* Payen. *Cours de Chimie Organique*.

The use made of gluten in the French manufactories, where the preceding process is carried on, is in the preparation of macaroni, vermicelli, &c., by mixture with a certain quantity of common flour. The quality of these preparations is considered to be nearly proportional to the quantity of gluten contained in the flour of which they are made. On that account the flour used for this purpose by the Italians is made from wheat imported from Africa, the grains of cereals grown in hot climates always containing more gluten than those of the same species grown in more temperate. To the French and Italians, who consume an immense quantity of these preparations, this application of gluten is of great importance, and probably contributes in a great degree to the success of the process just described as a commercial speculation.

Wheat is sometimes employed in the manufacture of starch in an unground state. Having been sifted clean, it is soaked in soft water until it becomes swollen, and so soft as to be easily crushed between the fingers. It is then taken out, and immersed for a short time in warm water; after which it is placed in bags, and exposed to strong pressure in a wooden chest containing some water. From the milky liquor which is thus obtained, the starch is procured by the successive steps described in the first process, or by the action of an alkali, as will afterwards appear.

Instead of pressing the swollen grain in bags, some manufacturers prefer to grind it between a pair of horizontal rollers, or under vertical edge-stones, and then to wash out the starch by repeatedly agitating the ground grain with water in a large cistern. As

soon as the heavier portions are subsided, the milky liquor is decanted, and the starch allowed to subside. It is probable that more gluten accompanies the starch made by this process, than when the grains are pressed in bags.

§ III. PREPARATION OF STARCH FROM RICE.*

A process for preparing starch from those grains in which it is accompanied by gluten, differing essentially in some respects from those which have just been considered, has been extensively practised, of late, by several manufacturers, and was introduced on the large scale by Mr. Orlando Jones in 1840. In this process, the separation of starch from gluten is effected by digesting the farinaceous matters in a dilute solution of an alkali. The gluten is thereby dissolved, and the starch left unacted on. The process is applied on the large scale,

* Analyses of Carolina rice and Piedmont rice by Braconnot afforded the following as the constituents :

	<i>Carolina.</i>	<i>Piedmont.</i>
Starch	85.07	83.80
Gluten	3.60	3.60
Gum	0.71	0.10
Uncrystallizable sugar	0.29	0.05
Colourless rancid fat, like suet	0.13	0.25
Vegetable fibre	4.80	4.80
Phosphate of lime	0.13	0.40
Water	5.00	7.00
	<hr/>	<hr/>
	99.73	100.00

Besides traces of chloride of potassium, phosphate of potash, sulphur, acetic acid, lime, and potash.

more particularly, to the preparation of starch from rice; but it may be also employed with advantage to prepare starch from wheaten flour. The impure deposit of starch obtained by washing dough (as in the process described at page 116) may be easily rendered pure by digestion in a dilute alkaline liquor. By this process not only may a larger quantity of excellent starch be obtained than by the common fermenting process from the same amount of grain, but the time required for production is materially shortened, and the bye-product, or gluten, may be made available for other purposes.

This is said to be the only process by which rice can be made practically available as a source of good starch.

The first part of Mr. Jones's process consists in the preparation of a solution of caustic potash, or caustic soda containing about two hundred grains of real alkali to the gallon. If much stronger, the alkali would dissolve the starch as well as the gluten. To every fifty gallons of the alkaline solution, one hundred pounds of rice are added, and allowed to macerate for from twenty to twenty-four hours. The vessel in which this mixture is digested may be of stone-ware, of tinned iron, or of tinned copper.

When the rice has digested the proper time, the alkaline solution of gluten is drawn off into a wooden vessel by means of a tin siphon or a tinned tap fixed to the bottom of the vessel, the interior opening of which is furnished with a piece of finely perforated tin or other strainer. The residuary rice is then washed by the affusion of a large quantity of cold

water, which is drawn off, and the rice set to drain on sieves.

When the rice is completely drained, it is reduced to flour by grinding with rollers or millstones, and after being passed through sieves, is digested a second time in an alkaline ley of the same strength as before, in the proportion of one hundred pounds of flour to one hundred gallons of ley. To this mixture is added any deposit which may have been formed in the water with which the starch was washed. The flour is repeatedly agitated during twenty-four hours, and then allowed to deposit for about seventy hours. The deposit consists of two layers, the lowest of which is composed of the fibrous matter of the grain with a little starch; the uppermost layer is starch. The supernatant solution, which is of a brownish-yellow colour, and more or less turbid, contains the whole of the gluten.

When the starch is completely deposited, the liquor is decanted, and the deposit is agitated with a large quantity of cold water. On standing for about an hour, the fibrous matter (which is deposited much quicker than the starch) falls to the bottom accompanied with a little starch, but leaving by far the greater quantity suspended in the liquor. The latter is then drawn off by a tin siphon, passed through a fine sieve to remove any portions of the husk with which it may be mixed, and received in a wooden cistern. The fibrous sediment is washed by repeated affusions of water and decantations so long as it continues to afford any starch.

The starch liquor in the wooden cistern is then allowed to settle for about seventy hours; and when

the deposition is complete, the liquor is decanted and the starch is blued, if required, drained, and dried in the usual manner.

Such is the process for preparing starch of the first quality from rice, but inferior starches may be procured from this source by less complicated modifications of Mr. Jones's process. Thus, for example, instead of separating the deposit of starch from the fibrous sediment by decantation, the mixture is sometimes agitated, and simply passed through a fine silk sieve to separate the husk, and received into a wooden tank where the final deposition takes place.

To obtain starch from wheat by the action of an alkali, Mr. Jones proceeds in the following manner, according to the specification of his patent.

The wheat being ground into meal as usual, fifty pounds of it are well mixed with one hundred gallons of caustic alkaline solution of the strength of one hundred grains of real alkali to the gallon: the mixture is repeatedly agitated during twelve hours, and then allowed to stand about seventy hours to subside. The deposit consists of three layers, the lowest of which is the bran; the middle layer is the fibrous matter, and the uppermost starch. The supernatant liquor, which is brownish-yellow, contains the gluten in solution with traces of foreign matters. When the deposition is complete, the liquor is decanted, and the deposit is mixed with fresh water, and passed through sieves to separate the bran. The separation of the starch from the fibrous matter is then effected in the same manner as in the process for rice starch.

To procure the gluten contained in the alkaline liquors of these operations, the alkali is carefully neutralized with sulphuric acid. The gluten is thereupon precipitated, and when completely subsided the clear supernatant liquor is decanted and the precipitate washed by affusion and decantation. It is afterwards drained, dried in stoves, and ground into flour by a mill or by rollers. It is said that the flour thus obtained may be advantageously mixed with wheaten flour in the preparation of bread, biscuit, &c. The fibrous matter separated in the manufacture of starch of the finest quality may be mixed with the gluten, and the whole dried and ground for use.

A process for making starch has been patented by Mr. Berger, in which the solvent for the gluten is a solution of a fixed alkaline carbonate; carbonate of soda being preferred, from its relative inexpensiveness. A hundredweight of unground rice, perfectly freed from the husk, is digested in water for two days, and then (the water being decanted) reduced to the consistence of thick cream by being passed with water through levigators, and strained through a sieve. To the pulp thus obtained is added a solution of carbonate of soda, composed of seven pounds of the carbonate dissolved in three and a half gallons of water, and the mixture is stirred for half an hour: it is then allowed to stand for fifty or sixty hours, being stirred once every four hours. At the end of that time the mixture is allowed to repose; and after having stood for twelve or eighteen hours, the supernatant liquor, contain-

ing the gluten, is decanted, and the sediment is treated in like manner with another solution of carbonate of soda of the same quantity and strength as before.

The sediment is next mixed with two hundred and twenty-four gallons of water, and the mixture is pumped slowly into a long vat divided into three or more compartments. When the first compartment is full, the liquor flows over the partition into the second; and so on until the vat is filled, and the liquor runs out at the farther end. By this arrangement, the heavy gritty particles with which the starch is mixed are separated in the different compartments, and the starch passes from the vat in a pure state. The liquor is allowed to stand, and the starch is separated and boxed in the ordinary manner.

An additional quantity of starch may be obtained by collecting the gritty sediments in the different compartments, and treating them in like manner with another quantity of the solution of carbonate of soda.

Another method of preparing starch from rice has been devised and patented by Mr. James Colman, which consists in the application of a dilute acid as a solvent for the gluten, the starch remaining undissolved. The acid to which preference is given is hydrochloric or muriatic. The rice, having been softened by digestion in water and reduced to a pulp, is mixed with dilute muriatic acid, composed of three quarters of an ounce, or one ounce, of strong acid to a gallon of water, in the proportion of two

pounds of rice to a gallon of dilute acid, and is allowed to digest during five days, being stirred every four hours. The mixture is next left to settle for eighteen hours; after which the liquor is decanted, and the sediment treated in a similar manner with another quantity of acid liquor, somewhat more dilute than the former. The starch thus obtained as the sediment is washed through sieves, and dried, as usual.

§ IV. PREPARATION OF STARCH FROM THE POTATOE.

The manufacture of starch from potatoes is carried on to a very large extent in France; not less than twelve millions of kilogrammes, or about twenty-six millions five hundred thousand pounds, being produced there annually.

In this country, also, potatoe starch has of late been manufactured in considerable quantity, and sold for food under a variety of imposing names. The basis of "Bright's Nutritive Farina" is potatoe starch, carefully prepared and slightly aromatized and coloured. The "Prince of Wales' Food," prepared by the Patent Farina Company, "Anderson's Soluble Starch," and some of that sold as "Indian Corn Starch," are merely potatoe starch with various slight additions to impart a flavour. The "potatoe flour" met with in some Italian warehouses in London is the same substance (Dr. Pereira).

The composition of the potatoe has often been made the subject of chemical investigation. The existence of starch in the tuber was discovered about

PREPARATION OF STARCH FROM THE POTATOE. 125

the middle of last century, and announced in the Swedish Transactions with a simple process for its preparation. Pearson, Lampadius, and Henry junr. have executed analyses of different kinds of potatoes; but the results which deserve most confidence are those obtained by Einhof. The different varieties contain the same ingredients, but the proportions vary considerably, as may be seen by the following table. The first six results were obtained by Einhof; the seventh by Henry, and the remainder by Lampadius.

COMPOSITION OF THE POTATOE.

Variety of potatoe.	Starchy fibrin.	Starch.	Vegetable Albumen.	Gum.	Acids and Salts.	Water.
1 Red potatoe	7·0	15·0	1·4	4·1	5·1	75·0
2 " after budding	6·8	15·2	1·3	3·7		73·0
3 The buds or germs ...	2·8	0·4	0·4	3·3		93·0
4 Kidney potatoe	8·8	9·1	0·8			81·3
5 Great red "	6·0	12·9	0·7			78·0
6 Sweet "	8·2	15·1	0·8			74·3
7 Paris "	6·79	13·3	0·92	3·3	1·4	73·12
8 Peruvian "	5·2	15·0	1·9	1·9		76·0
9 English "	6·8	12·9	1·1	1·7		77·5
10 Onion "	8·4	18·7	0·9	1·7		70·3
11 Voigtland "	7·1	15·4	1·2	2·0		74·3

The potatoe contains some substances, however, which are not included in the preceding table. An extended analysis by Michaëlis (in 1837) of a red potatoe, richer in starch than the ordinary varieties, gave the following results:

Starch	}	30.469
Starchy fibrin			
Albumen	503
Gluten	055
Fat	056
Gum	020
Asparagin	063
Extractive matter	921
Citrates, silicates, and phosphates of potash, soda, lime, magnesia, alumina, and protoxides of iron and manganese	}815
Chloride of potassium			
Free citric acid	047
Water		66.875
			100.000

The *starchy fibrin* or *amylaceous fibrin* of the potatoe differs essentially from the fibrous matter of most plants. It consists for the most part of a substance analogous to common starch in many of its properties. *Asparagin* is a white, soluble, crystallizable substance discovered in the juice of the asparagus by Robiquet in 1805. It was first detected in the potatoe by Vauquelin.

The shoots of germinating potatoes were discovered by M. Baup to contain a small quantity of *solanine*, an extremely poisonous substance which constitutes the active ingredient of the *solanum dulcamara* (deadly night-shade). It is contained in several species of *solanum*. The observation of Baup has been confirmed by Otto of Brunswick, who found the germs developed in the spring to contain a very sensible quantity of this poisonous principle. The tuber itself sometimes contains a small quantity, which it readily yields to water (Buchner). If germinated potatoes (with the germs remaining) are employed in the preparation of po-

tatoe spirit, the residue contains so large a quantity of solanine, that cattle fed with it become paralyzed in their posterior extremities.*

From the table inserted at page 125, it is evident that different varieties of the potatoe contain very different quantities of starch. The following table, drawn up from the experiments of Mr. W. Skrimshire, shews the proportion of starch, &c. obtained from five pounds of various kinds of fresh potatoes. The starch was separated by grating the potatoe and washing the pulp on a searce (Thomson's Organic Chemistry, Vegetables).

STARCH IN POTATOES.

Ingredients.	Kinds of Potatoes.									
	Captain Hart.		Rough red.		White kidney.		Moulton white.		Yorkshire kidney.	
	lb.	oz.	lb.	oz.	lb.	oz.	lb.	oz.	lb.	oz.
Fine starch	0	9	0	7 $\frac{1}{2}$	0	0	0	9	0	8 $\frac{3}{4}$
Ditto slightly coloured	0	3	0	3 $\frac{1}{2}$	0	9 $\frac{1}{2}$	0	2 $\frac{3}{4}$	0	2 $\frac{1}{2}$
Pulp dried	0	6	0	6 $\frac{1}{2}$	0	3 $\frac{3}{4}$	0	5 $\frac{3}{4}$	0	6 $\frac{1}{2}$
Water, mucus, and extractive..... }	3	14	3	15	4	2 $\frac{3}{4}$	3	14 $\frac{1}{2}$	4	0 $\frac{1}{4}$
Total	5	0	5	0	5	0	5	0	5	0

* This is by no means a rare instance of the contiguity of an active poison and an amylaceous substance. In the tuber of Arum, for instance, starch is associated with an acrid principle which gives it a purgative property; and in the root of the *manioc*, from which tapioca and cassava are prepared, the starch is accompanied by prussic acid. But, fortunately, the poisonous matters may always be removed by

The relative quantity of starch, however, depends not only on the variety of potatoe, but on the nature of the soil, the mode of culture, and the season of the year at which it is prepared. That the same kind of potatoe contains different proportions of starch at different seasons of the year, has been lately shewn by M. Pfaff, who obtained the following quantities from 240 pounds of the same kind of potatoe:*

In August, from 23 to 25 pounds ;
In September, from 32 to 38 pounds ;
In October, from 32 to 40 pounds ;
From November to March, from 38 to 45 pounds ;
In April, from 38 to 28 pounds ;
In May, from 28 to 20 pounds.

As the proportion of starch is so variable, the manufacturer should always make a preliminary estimation on a small scale of the value of the potatoe to be used in the manufacture, before appropriating a considerable quantity for that purpose. To determine the real value of the potatoe, it is necessary to know, 1°, the amount of water ; and 2°, the amount of starch in the dry residue.

The proportion of water may be determined with sufficient accuracy in the following simple manner. The potatoe being well cleaned is cut into very thin

extremely simple means. They are invariably soluble with facility in water ; hence the process of washing in cold water suffices for their removal. The inhabitants of Guyana and the Antilles have long been acquainted with the means of separating the prussic acid from the starch deposited from the juice of the manioc. Their method consists in exposing the starch to a moderate heat ; when the prussic acid, which is extremely volatile, is entirely dissipated in vapour.

* According to M. Girardin, frosted potatoes afford as much starch as those which are unfrosted.

lices, which are weighed and then placed side by side on a plate, and covered with a piece of bibulous paper. The slices are then exposed to a moderate heat (about 110° or 120° Fahr.) in a drying stove or other convenient place. The completion of the drying is known by the weight of the slices remaining constant after intervals of a quarter of an hour or so. They are then hard and brittle, and the loss on their original weight gives the proportion of water required.

The amount of starch is estimated by a process quite analogous to that practised for its extraction on the large scale. A fresh quantity of washed potatoes is reduced to a fine pulp, with the assistance of a rasp, weighed, and placed on a fine sieve of horse-hair or metallic gauze. A small stream of water is allowed to fall on the centre of the sieve, the pulp being at the same time briskly agitated between the hands. This operation is continued so long as the water passes through the sieve in a milky state. The starch liberated by the rupture of the vegetable cells is carried by the water through the sieve, and is deposited on the standing of the milky liquid. When fully subsided, the supernatant liquid is poured off, the starch agitated with a fresh quantity of water, and again allowed to subside: the decantation and affusion of fresh water having been repeated two or three times, the starch may be drained, carefully dried in a stove, and weighed.

As the starch is not distributed over the tuber equally, in making such an analysis as this the part operated on is not a matter of indifference. The starch is contained in largest quantity towards the

exterior ; sometimes, especially in large potatoes, the centre is almost transparent, from containing nothing besides cellular tissue and water. Immediately under the epidermis, however, is situated a thin layer or zone of cellular tissue devoid of starch ; the tissue immediately underneath this contains the starch in large quantity, and the proportion decreases gradually towards the centre (M. Payen). Hence, to obtain a sample representing the true composition of the tuber, the slices should be cut in such a manner as to contain a fair proportion of each of the layers.

The process of preparing potatoe starch on the large scale, about to be described, is that followed in the principal establishments in France, where this manufacture is conducted on a more extensive scale than in England. I am chiefly indebted for the description of it to the *Cours de Chimie Organique* of M. Payen (1842).

In keeping potatoes in store before they are required for use, care should be taken to preserve them from the influence of any agents which are favourable to the decay or to the germination of the tuber. Potatoes have been preserved for a whole year in an ice-house at the temperature of the freezing point of water without any sensible loss in their proportion of starch. It was common formerly to keep them in heaps in subterranean cellars, but this plan is not approved of now, as potatoes thus kept are very subject to a fermentation excited originally by bruises on the surface, and favoured by the retention of the heat thereby developed. The common method of preserving potatoes followed at present is to imbed them in large shallow ditches

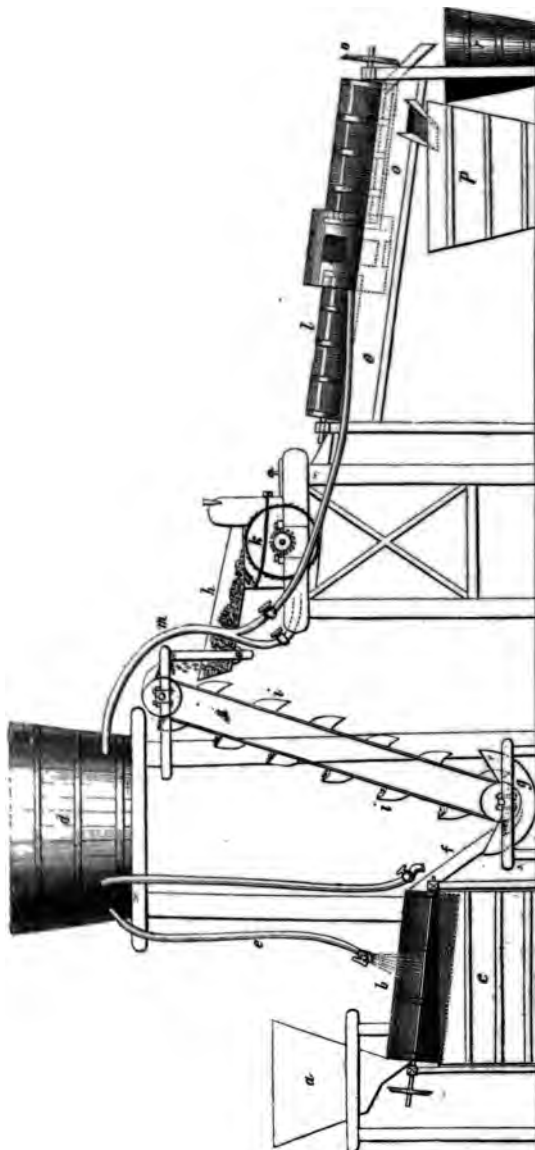
(*silos*), dug, if possible, in a sandy soil. They should be situated near the starch-works, and be protected from the access of air by a thatched straw or other covering. To avoid or lessen the fermentation referred to, the ditch should be provided with small apertures to serve as ventilating chimneys, by which the heated air and gases may escape. These apertures may be made by planting some dry chat-wood in the mass.

The form of apparatus generally employed at present in the manufacture may be understood with the assistance of the design in the following page. It consists essentially of three parts; a washing cylinder for the potatoe, a rasping machine, and a sieve.

1. An indispensable preliminary operation in the manufacture is the soaking of the potatoes for about six hours in water, the object of which is to soften the epidermis, and thus facilitate its removal. They are then transferred through the hopper *a*, to a cylindrical cage *b*, and washed by revolving the cage in a trough of water *c*, a jet of water flowing at the same time from the cistern *d*, through the pipe *e*. All the earthy matter, and a great portion of the skin itself, are separated by the friction of the potatoes against each other. In one French manufactory the potatoes are washed in two cylinders successively.

2. The next operation consists in the reduction of the potatoes to a fine pulp. This is a process of much importance, as the quantity of the product of starch depends in a great measure on the amount of disintegration of the cellular tissue.

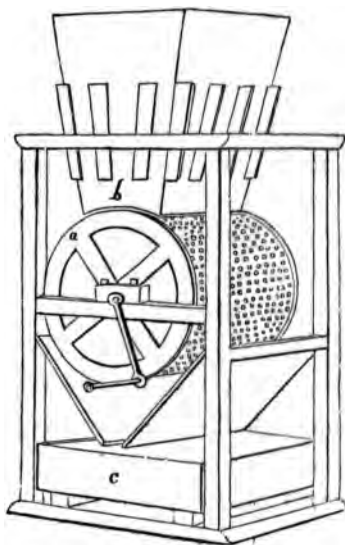
Fig. 27.



After being washed in the cylinder, the potatoes are passed through the conduit *f*, to the trough *g*, from whence they are elevated to *h* by means of the endless chain *i i*, furnished with cups. The potatoes then fall into the chest containing the rasping machine *k*, and passing under the circular rasp are reduced to a pulp, which is conducted into the cylinder sieve *l*, to be washed. A moderate stream of water is made to play against the surface of the rasp, to prevent the notches on its surface from becoming clogged, and to wash the pulp into the cylinder. The water is supplied from the cistern by one of the limbs of the tube *m*.

Fig. 28.

Any kind of circular rasp may be employed, provided it can be made to work rapidly. The general construction may be understood by reference to fig. 28. The rasp itself *a* is a wooden drum covered on its circumference with sheet-iron roughened outside by several prominences made by punching holes from the opposite side. The bottom of the hopper *b* is concentric and nearly in contact with



the rasp. The pulp falls into the chest *c*. The number of revolutions made per minute with a good rasp should be nine hundred or a thousand.

The quicker the rasp is turned, the greater is the effect produced with the expenditure of the same amount of force.

3. The rasping being effected, the next operation consists in washing the pulp on a sieve to separate the starch from the cellular tissue. For this purpose the pulp is generally conducted into a cylindrical sieve of metallic gauze composed of three pieces of unequal diameters, as represented in the figure. The cylinders are revolved by a winch at *n*. Fresh water enters the cylinders from the cistern by the tube *m*, and the milky liquid which falls from the sieve to the bottom of the box *o* is conducted into the trough *p*; the washed pulp is received into the bucket *r*.

4. The starch soon subsides from the liquor, and forms a coherent layer from which the supernatant liquid may be easily poured off. Notwithstanding the careful washing of the potatoes at the commencement of the process, the first deposit of starch always contains a little sand, which is easily separated by affusions of water and decantations. After agitating the impure starch with water, the sand being the heavier immediately subsides; the milky liquid is transferred to another vessel, where the starch is deposited almost wholly freed from sand. After having been again washed to remove a light albuminous matter which lies over the deposit of starch, it is placed to drain on cloths in small trays, the bottoms of which are pierced with holes; and when the greater part of the water is drained off, the trays are placed on a floor composed of pieces of well-dried plaster. This material having a great avidity for water, rapidly

absorbs it from the starch, so that the latter in a few minutes becomes quite firm, friable, and hardly feels moist. The starch is sometimes sent to market without any further drying, being sold in that state under the name of "green fecula." It generally contains about 38 per cent. of water, and is used in the preparation of dextrin and starch syrup, and for other purposes.

5. To obtain the starch in a dry state, after having remained for twenty-four hours on the floor of plaster, it is cut up into blocks or broken into small lumps and placed on shelves in a well-ventilated drying-house. The masses are turned over occasionally to accelerate and equalize the desiccation, and when they begin to crack are transferred to a hot stove, where the drying is completed. A current of hot air enters the stove at top, and passes out at bottom. The starch is heated to a temperature between 131° and 136° Fahr. (55° and 58° Cent.). It is occasionally stirred with a wooden spatula to expose fresh surfaces and to prevent the formation of small hard lumps, and when sufficiently dry is passed through a silken sieve. The matters which remain on the sieve are ground under a roller, and again sifted to avoid any loss of starch.*

The dry potatoe starch met with in commerce is far from being entirely free from moisture. The quantity of water in it varies according to the temperature and the humidity of the air, but generally amounts to one-fifth of the weight of the starch. According to M. Payen, potatoe starch absorbs water

* Payen, *Cours de Chimie Organique*, t. i. p. 117.

from an atmosphere perfectly saturated with moisture, until it has acquired 23 per cent. It is much more hygrometric than other kinds of starch, and hence not so well adapted for stiffening linen, &c.

Potatoe starch is often adulterated with gypsum, chalk, and argillaceous substances. Sophistication from either of these sources may be easily detected by burning a small quantity of the suspected starch, and incinerating the ash. Unadulterated starch leaves the merest trace of earthy matter.

The starch of potatoes, like all other kinds of starch, is unfit alone for the preparation of pastry; but a small proportion of potatoes or of potatoe starch, added to wheaten flour, is considered by some to improve the quality of bread. If the proportion of potatoe starch exceeds one-fifth of the weight of the flour, a peculiar flavour is communicated to the bread, arising from a minute quantity of an oily matter contained in several amylaceous principles, which is supposed by M. Payen to be identical with the oil of potatoe spirit or fousel oil. This substance was discovered by Scheele in brandy obtained by distilling fermented potatoes, and has lately been made the subject of investigation by several chemists. It is a colourless oily liquid possessing a very powerful odour, at first rather agreeable, but immediately afterwards nauseous in the highest degree. This substance is generally believed to be a product of the fermentation of the potatoe, and not to pre-exist in the tuber, as supposed by M. Payen. It has been lately observed that the last syrup obtained in the manufacture of beet-root sugar, produces, when fermented and distilled, a considerable quantity of

fousel oil. If such be the case, its formation during the process of fermentation hardly admits of doubt. If potatoe starch is washed first with tasteless alcohol, and afterwards with cold water, it may be entirely deprived of its peculiar flavour, and loses in weight at the same time about one part in two thousand.

The principal uses of potatoe starch, besides those referred to at page 124, are in the preparation of grape or starch sugar, and British gum or dextrin for the use of the calico-printer, to both of which applications we shall again have occasion to advert. It is also at present employed to a considerable extent as a substitute for glue in the preparation of size for paper, being usually mixed for that purpose with a small quantity of a solution of resin with carbonate of soda in water. This application of starch may be easily detected by moistening the paper with an aqueous solution of iodine, when the blue iodide of starch will be formed if any starch is present (page 108). A variety of tapioca is prepared from potatoe starch by heating the moistened fecula on a copper-plate to near the temperature of the boiling point of water. Some of the granules of starch then burst, agglomerate, and form small, hard, and irregular grains, which closely resemble the true tapioca. It is said that potatoe starch prepared in October or November is more easily digested than that made in the spring.

The bye-products of the potatoe starch manufacture are not without their applications. Thus, the water from which the starch is deposited (starch-water) is well adapted for irrigation; it contains

the débris of the pulp, and holds in solution six parts in a thousand of azotized matter. It was formerly an inconvenience to the manufacturer, as it contains a poisonous substance, and produces an evolution of sulphuretted hydrogen gas if kept a short time, from the decomposition of sulphates by the organic matter. The marc of the pulp which remains after the extraction of the starch is made use of in various ways as food for cows and sheep. It must first be deprived of about half its weight of water by expression, for, if simply drained, it retains too much water to be advantageously eaten by cattle in large quantities.*

A few years ago potatoe starch was employed to a pretty large extent to adulterate wheat starch, and the price of the former was then so low that a profit of twenty-five per cent. was realized by the sophistication. But since the numerous applications of potatoe starch have increased the value of this substance, the sophistication has not, I believe, been practised. The presence of potatoe starch in wheat starch is very easy of detection by the microscope,

* As an application of the great quantity of pulp produced in extensive works may not be always at command, it is important to the manufacturer to have the means of securing its preservation. To that end, some add a small quantity of common salt, then bury the mixture in heaps and cover it with a straw thatch ; but such a mass is very subject to fermentation, which rapidly renders the whole useless. A more effectual method is to dry the pulp thoroughly by exposing it to a moderate temperature. It may then be preserved in granaries for a twelvemonth or more, and merely requires moistening with a little water to be fit for consumption by cattle with avidity. In seasons when fresh alimentary vegetables are abundant, the pulp may be employed as manure, especially as it then contains a small quantity of solanine (page 126), and cannot therefore be given to cattle with impunity.

although the proportion of the former does not exceed two per cent. Potatoe starch is sold in the shops as "English arrow-root."

§ V. ARROW-ROOT ; SAGO ; TAPIOCA ; SALEP ; TOUS LES MOIS ; AND INDIAN-CORN STARCH.

Arrow-root.—Such is the inappropriate designation of a very pure starch, derived chiefly from the tubers of the *maranta arundinacea** (a native of South America and Jamaica), and in part from the *maranta indica*. The mashed root of the former plant is applied by the native Indians to wounds from poisoned arrows; hence the English designation of its fecula.

To prepare arrow-root, the tubers are dug when a year old, well washed, and beaten to a thin pulp in deep wooden mortars. The pulp is washed in clean water, and the fibrous matter of the root is wrung out by the hands and thrown away. The milky liquor containing the starch is passed through a coarse cloth and allowed to deposit its fecula. The water is drawn off, and the starch washed by re-

* The composition of the root of the *maranta arundinacea* has been examined by M. Bonzon. He found the fresh root to contain :

Starch	26·00
Vegetable albumen	1·58
Gummy extract	·60
Volatile oil	·07
Chloride of calcium	·25
Fibrin	6·00
Water	65·50
	<hr/>
	100·00

peated affusions of water and decantations until it is quite clean, when it is laid out before the sun to dry.*

Arrow-root, when dissolved in an appropriate vehicle, is considered to be more digestible than the starch of wheat or potatoes. It is exported from most of the West India Islands in tin cases and in barrels and boxes. The most esteemed is that brought from Bermuda. The adulteration of arrow-root with potatoe starch may be detected by the microscope.†

A variety of starch obtained from the tubers of the narrow-leaved turmeric (*Curcuma angustifolia*, Roxburgh) is imported into this country from Calcutta, Para, Maranhão, and Sierra Leone, under the name of East Indian arrow-root. Two kinds are met with in commerce, the *white* and the *pale buff-coloured*. The first is a fine white powder, readily distinguishable, both by the eye and touch, from West Indian arrow-root. In appearance it somewhat resembles a finely powdered salt (as bicarbonate of soda or Rochelle salt). The pale buff-coloured East Indian arrow-root is in the form of powder or pulverulent masses, mixed with husks, woody fibre, and other impurities. Both kinds present the same appearance under the microscope.

The fecula known as Brazilian arrow-root is obtained from the tuberous root of the *Jatropha manihot*; and the "Portland arrow-root" is derived from the *arum maculatum*.

* London Medical Journal, vol. viii. Wright.

† The particular microscopic characters of these and other kinds of starch will be found at pages 144, 145.

Sago.—This is a variety of starch derived from the pith or medulla of true palms of the genus *Sagus*, especially the *Sagus farinifera*. In the Moluccas, sago is procured in the following manner (Pereira's *Materia Medica*). When the tree is sufficiently mature, it is cut down near the roots, and the trunk is subdivided into portions of six or seven feet in length, each of which is split into two parts. The medullary matter is extracted, reduced to powder, and mixed with water. The mixture is strained on a sieve, and the milky percolated liquor is allowed to stand to deposit the starch, which is fit for use after two or threeedulcorations. This is "sago-meal" or "pulverulent sago," which scarcely ever reaches this country. It is a fine white powder much resembling arrow-root.

To make the "common" or "brown sago," the finest meal is mixed with water, and the paste is rubbed into the small grains, in which state it is met with in commerce. When examined by the microscope, the granules are found to be perfect. "Pearl sago" is probably made by drying a paste of sago-meal over a fire with agitation. The grains of pearl sago are smaller than those of common sago, and the granules of the former are found to be ruptured when examined by the microscope. They hence swell up when digested in cold water, and a small portion dissolves. The filtered liquid gives a blue colour with iodine, but a cold filtered infusion of brown sago or pulverulent sago undergoes no change on the addition of a solution of iodine.

The sago-palm contains the largest quantity of starch just before the evolution of the flower-bud.

A single tree often affords five or six hundred pounds of sago.

Cassava and Tapioca.—Cassava is a variety of starch imported into this country from South America, the West Indies, and some parts of the coast of Africa. It is derived from the tuberous roots of the *Jatropha manihot* or *manioc*, a native of Brazil. The peeled roots are reduced to a pulp, and expressed in canvas bags to separate most of its poisonous juice.* The squeezed mass is dried at a moderate heat, by which its poisonous principle (hydrocyanic acid, according to M. Henry) is entirely expelled, and the mass concretes into hard lumps. These, when reduced to a pulverulent state, constitute "cassava powder" (*farine de manioc*), and when baked into cakes on earthen or iron plates, form cassava bread, which is one of the most important articles of the negroes' food.

The expressed juice of the tubers of the *Jatropha manihot* gradually deposits a quantity of fecula, which may be easily obtained pure by repeated washings. When dried in the air without heat, it is termed *moussache* or *cipipa*, and has been lately imported into Europe and sold under the name of Brazilian arrow-root. The granules of *moussache* are much smaller and more spherical than those of arrow-root. When the fecula is dried on hot plates with agitation, it agglomerates into little granular masses, and then constitutes *tapioca*, which is one of the purest forms of starch met with in commerce.

* The expressed juice is employed by the Indians to poison their arrows; when distilled, it affords a considerable quantity of hydrocyanic acid.

It is slightly soluble in cold water, and the solution strikes a blue colour with iodine, which shews the rupture of some of the starch granules in the preparation of this substance. But most of the granules remain uninjured, and when examined by the microscope are found to be spherical, of nearly equal volume, and smaller than those of arrow-root or the average of wheat starch.

Salep or Saloup.—This amylaceous substance is the dried and prepared tuberous roots of several plants of the orchis tribe, formerly imported to a considerable extent from Persia and Asia Minor, but which has now almost ceased to be an article of commerce in this country. It is met with in small oval grains of a whitish-yellow colour, composed almost entirely of starch. A very good salep may be procured from the *orchis mascula*, *orchis latifolia*, and other plants of this order, which grow wild in Britain. The tubers should be washed with fresh warm water, scraped, and boiled in water for a quarter of an hour or twenty minutes (or until they begin to afford a mucilage), and then dried either by exposure to the sun or in a drying stove. The salep thus obtained is said to be equal to that from Turkey.

Tous les mois.—A starch, known by this name, has been imported from the West Indies, particularly from the Island of St. Kitt's, within the last few years, said to be prepared by a tedious process from the root of the *canna coccinea*, which is a species of fir-tree. The granules of this starch are very large, even larger than those of potatoe starch, with which they agree in form. It is a very pure substance, and having no unpleasant flavour has been

recommended as forming an agreeable article of food for the invalid.

Indian corn starch.—A recent patent for some improvements in the manufacture of starch, obtained by Mr. Colman, includes an application of the process of Mr. Jones for preparing starch from rice, &c., to its preparation from maize or Indian corn. The proportions of the materials employed are a pound of starch to a gallon of alkaline solution, containing two hundred grains of caustic potash or caustic soda. Carbonate of soda or of potash is sometimes substituted for the caustic alkali. This process closely resembles in its details that of Mr. Jones. A process is also described by Mr. Colman for procuring starch from Indian corn by fermentation, which requires about fifteen days for its completion.*

* As the only satisfactory method of distinguishing between the different varieties of starch is by subjecting them to an examination by the microscope, the following account of the microscopic characters of the starches afforded by several different plants may prove useful.

Starch from potatoes.—With the exception of tous les mois, the granules of potatoe starch are larger than those of any other kind. Their form is rather varied, but commonly as shewn in fig. 20, page 101. The elliptical rings are unusually distinct in potatoe starch. The common size of the granules is from $\frac{1}{400}$ to $\frac{1}{300}$ of an inch in diameter. The cross and supplementary colours by polarized light are very distinct.

Sago.—The granules of sago-meal or pulverulent sago are somewhat rounder than those of most other kinds of starch. Their size is pretty uniform, and about the $\frac{1}{400}$ of an inch in diameter. Most of the granules of pearl sago are ruptured, but those of brown sago are perfect. The cross by polarized light is very distinct.

Starch of oats.—That which appears to be a large granule of oat starch when examined by a power of one hundred diameters, proves with a higher power to be a glutinous cell, to which small granules of starch are attached, the diameter of which is about $\frac{1}{400}$ of an inch.

Starch of the kidney bean.—The granules are ovoid and have a point on one side. The diameter of the largest is about $\frac{1}{400}$ of an inch.

§ VI. DEXTRIN AND STARCH SUGAR.

By the action of dilute acids at a moderate temperature, and also of a particular azotised substance contained in germinated seeds, starch becomes converted into a fermentable sugar, resembling, but not identical with, cane sugar.

The discovery of this effect of dilute acids was made by M. Kirchoff, a chemist of Petersburg, at the time of the exclusion, by Napoleon, of colonial produce from Russia, during the enforcement of the Continental System. Kirchoff was rewarded by the Emperor of Russia with an annuity of a thousand roubles. The discovery soon attracted considerable attention in a commercial point of view; many im-

Wheat starch.—The granules rarely exceed $\frac{1}{300}$ of an inch in diameter: they are spherical, and when prepared from flour, are often accompanied by the teguments of broken granules. Wheat starch does not exhibit the cross by polarized light as distinctly as most other starches.

Starch of barley.—The granules are about the same size as those of wheat starch, and almost circular. The cross by polarized light is not very distinct.

Starch of rye.—The largest granules of this starch have a diameter of $\frac{1}{200}$ of an inch. They are flattened, and generally marked on one of their faces by a small black cross or by three black rays proceeding from the hilum of the granule (Raspail).

Starch from the bean.—The usual size of the granules is $\frac{1}{200}$ of an inch in diameter. They are ovoid or reniform.

Starch from green peas.—The granules have the same form as those of potatoe starch, and a diameter of about $\frac{1}{200}$ of an inch (Raspail).

Arrow-root.—The granules of arrow-root are not so spherical as most other starches, being generally flattened at one end. The spherical lines are not so well defined as in *tous les mois* and potatoe starch, but the cross by polarized light is very distinct. The diameter of the largest globules is about $\frac{1}{100}$ of an inch.

Starch of the horse-chestnut.—The form of the granules is very irre-

provements in the details of the original process were introduced; and the preparation of starch sugar soon became, on the Continent, a profitable and important manufacture.

The acid generally employed in this process is the sulphuric, as being the cheapest; but oxalic acid seems to be preferable. The following is a brief outline of the process as conducted in the French establishments.

In the first place, a mixture of ten kilogrammes of oil of vitriol, specific gravity 1·848, and twenty kilogrammes of water is added to a thousand kilogrammes of water at the boiling temperature in a leaden boiler. The liquid being again heated to ebullition, one workman gives it a circular movement with a stirrer, while another adds four hundred kilogrammes of starch, by very small quantities at a time, so that the ebullition is not allowed to cease, nor anything like a jelly to be formed. In this way each portion of the starch is converted into sugar

gular. Their longest diameter is about $\frac{1}{1000}$ of an inch, but varies considerably according to the size and age of the nut.

Starch of the tapioca plant or tapioca meal.—The granules are spherical, equal in size, and about $\frac{1}{500}$ of an inch in diameter. The hilum is very distinct, as well as the cross and colours, by polarized light.

Russian semolina.—A few of the granules are ruptured. The perfect granules are spherical, and about $\frac{1}{500}$ of an inch in diameter. The cross by polarized light is not shewn distinctly by this variety of starch.

Indian corn starch.—The granules are almost perfectly spherical, and the diameter of the largest does not exceed $\frac{1}{500}$ of an inch. The cross with polarized light is very clear.

Starch of the orchis tribe.—Before the root is converted into salep by ebullition, the granules appear perfectly spherical, and the diameter of the largest is no more than $\frac{1}{3500}$ of an inch (Raspail).

Starch of the millet.—The granules of this starch are the smallest Raspail has observed, being only $\frac{1}{10000}$ of an inch in diameter.

almost immediately on its introduction. The ebullition is continued for eight or ten minutes after the last addition of starch : the solution should then be quite fluid and almost transparent.

The source of heat being withdrawn from the boiler, the acid is neutralized by chalk, which is added in slight excess ; the sulphate of lime thus formed is allowed to deposit, and the supernatant solution is transferred by a siphon-tube to a filter of animal charcoal supported on a linen cloth. The animal charcoal serves to withdraw a considerable portion of the colouring matter in the solution.

If the sugar is required in the state of syrup, the filtered liquid is evaporated until of the specific gravity 1.261 (30° Baumé); but if the sugar is wanted in the solid state, the evaporation is carried to 1.333 (36° Baumé), or even to a greater density. On standing for a day or two the syrup deposits granular crystals, which are removed from the liquid, drained, and dried in a stove. The syrup itself is an article of commerce in France, being employed to mix with various saccharine liquors which are to be fermented. It is only within the last three or four years that the manufacture of starch sugar has been carried on in this country, and is now practised chiefly with a view of adulterating cane sugar.

The action of the sulphuric acid in this process is involved in much obscurity. The acid undergoes no diminution in quantity, there is neither absorption nor disengagement of gas, and the weight of the product of sugar exceeds the weight of the starch

employed. The only change undergone by the starch is the assimilation of a certain amount of water : the formula of crystallized starch sugar is $C_{12} H_{14} O_{14}$, and when dried at 212° , $C_{12} H_{12} O_{12}$: now the latter formula differs from that of starch only in containing two equivalents more of water, or at least of hydrogen and oxygen in the same proportions as in water. By calculation, one hundred parts of pure starch should afford one hundred and twenty-two parts of crystallized sugar; but so large a quantity is rarely, if ever, procured on the large scale. According to the observations of M. Fremy, a variable quantity of mannite (the saccharine principle of manna) is always formed in the transformation of starch into sugar.

Starch sugar is the sweet principle of grapes, and is hence commonly called *grape sugar*. It is also contained in figs, in almost all acid fruits, in honey, and in diabetic urine. By the action of dilute acids, several substances besides starch may be converted into starch sugar; among which are cane sugar, woody fibre, and sugar of milk. Starch sugar does not crystallize so well as cane sugar, and two parts and a half are required to produce the same sweetening effect as one part of cane sugar. From an alcoholic solution it may be crystallized in square tables and cubes. It is not so soluble as cane sugar in cold water, but dissolves in all proportions in boiling water.

As starch sugar is so much less sweet than cane sugar, it is important to have the means of detecting the sophistication of the latter by the former; a fraud which has been lately practised in this

country to a shameful extent. An excellent test to discriminate between the two sugars is a solution of sulphate of copper. If a saturated solution of that salt is added, drop by drop, to a solution of starch sugar mixed with a little caustic potash, a dark blue liquid is produced; which, in the course of a few minutes, affords a yellowish-brown precipitate of hydrated suboxide of copper, even when cold. But if the blue liquid is heated in a test-tube, flask, or other convenient vessel, decomposition takes place immediately, even before the mixture reaches the boiling point; the whole of the copper is precipitated, and the supernatant liquor remains colourless. According to M. Trommer, the discoverer of this excellent test, a solution containing no more than a hundred-thousandth part of starch sugar affords a sensible yellowish-red precipitate.

When a solution of sulphate of copper is added by drops to an alkaline solution of cane sugar, a dark blue liquor is likewise produced; but if the caustic alkali is in excess, no suboxide of copper is precipitated in the cold, nor even on boiling the solution for a short time. If the suspected sugar, therefore, when examined by this test, is found to afford a sensible precipitate of suboxide in the cold after standing for a few minutes, or immediately on the application of heat, there is abundant evidence to conclude that sophistication has been practised.

The conversion of starch into sugar does not take place immediately. An intermediate substance is formed, of the nature of gum or mucilage, which has

received the name of dextrin or mucilaginous starch. When pure, this substance is white, inodorous, tasteless, and largely soluble in water both hot and cold. The solution is mucilaginous, and not gelatinous, and closely resembles a gum.

The name of dextrin was applied to this substance by M. Biot, from the effect of its solution upon a ray of polarized light. It causes the plane of polarization to deviate to the right; in which respect it differs from common gum, which causes a deviation of the ray in the opposite direction. Dextrin itself is not fermentable by yeast; but by the action of acids and the azotised substance in germinated grains called *diastase*, it is readily convertible into starch sugar which is fermentable.

In France, dextrin forms an important article of commerce; it being susceptible of nearly all the applications of gum arabic, while it may be obtained at one-half the price of the latter. In this country it is also consumed in considerable quantities, chiefly in calico print-works, as a thickening material for colours, and is sold under the name of British gum.

For commercial purposes, dextrin may be prepared by the action of germinated barley or malt on starch. From 350 to 400 parts of water are heated to between 77° and 86° Fahr.; from 5 to 10 parts of dry malt are then added, and the heat is increased to 140°. At that temperature 100 parts of starch are added, the mixture is well agitated, and its temperature maintained between 150° and 167° Fahr., for twenty minutes. From being viscid and milky, it becomes almost as fluid as water, the

starch having undergone an obvious chemical change by the action of the malt. To prevent the further action of the diastase of the malt, which would consist in the conversion of the dextrin into sugar, the liquid is heated rapidly to its boiling point, then cooled, filtered, and evaporated to the consistence of a thick syrup. By cooling, it becomes an opaque gelatinous mass, which, when dried, is hard and brittle. The substance thus prepared is used on the Continent in calico-printing as a thickening material.

Starch is capable of being converted into dextrin by the action of heat alone, in which manner British gum is prepared for the use of calico-printers. For this purpose, starch is placed in oblong trays of sheet-iron, and heated to the temperature of 300° Fahr. in a cast-iron oven, capable of holding four of the trays. The granules of starch thereby become ruptured, and agglomerate into irregular, translucent, yellowish-brown lumps, which are merely ground into fine flour between millstones before being sent to market. It has been proposed to apply to starch a temperature of 390° Fahr. by means of an oil-bath. The conversion of the starch into dextrin or British gum is generally assisted, however, by the addition of a minute quantity of nitric acid; but this is by no means essential.*

As might have been anticipated from the preceding statement, a portion of the starch of flour

* Several different kinds of roasted or calcined starch are employed by calico-printers. Though these are the same substance, chemically speaking, if the torrefaction is properly conducted, yet slight differences may be detected in their mechanical state, which are of great importance in the application they receive in calico-printing.

is always converted into dextrin during the process of panification. From wheaten bread, M. Vogel obtained eighteen per cent. of dextrin.

The solution of dextrin was supposed to give no particular indication with iodine; but M. Jacquelin has observed that it gives either a purple colour (not a blue colour like starch), or no colour at all, according to the circumstances of its preparation. When first formed from starch by the action of an acid, it strikes a purple colour with iodine; but not after boiling for a short time, though not yet converted into sugar. It would hence appear that two varieties of dextrin exist; the one colourable by iodine, the other not colourable. The composition of dextrin was found by M. Payen to be identical with that of starch dried at 212° ; that is, $C_{12} H_{10} O_{10}$. A single equivalent of water may be displaced by several metallic oxides, so that the composition of anhydrous dextrin is probably $C_{12} H_9 O_9$. To obtain dextrin in a state of purity, a strong aqueous solution, obtained either by diastase or by sulphuric acid, is mixed with alcohol, when dextrin, which is insoluble in alcohol, is precipitated as a white glutinous substance, which becomes pulverulent by being washed with alcohol.

In the ordinary process of malting barley, in the kiln-drying, and in the mashing or infusing of the malt, starch is converted into sugar by the action of *diastase*. This remarkable substance was observed by Payen and Persoz in germinated grains, and in the tubers of the potatoe near the places from whence the sprouts proceed. To prepare it, germi-

nated barley is moistened with half its weight of cold water, and the mixture is submitted to pressure. The viscid liquid which is thus obtained is filtered, and heated to 158° (but not higher), in order to coagulate an albuminous matter existing in the solution, and after a second filtration is mixed with a quantity of alcohol. Diastase is thereupon precipitated as a white powder, soluble in water, but insoluble in alcohol; it may be purified by repeated solution in water, and precipitation by alcohol.

Diastase contains nitrogen, and is probably closely related to gluten, but its composition in a state of purity is unknown.

The principal object in the malting of barley, or allowing it to germinate, is the production of diastase. The process consists essentially of three successive operations: 1, the steeping the grain in water; 2, the couching, sweating, and flooring; and 3, the kiln-drying. The steep generally lasts from forty to fifty hours, according to the nature of the grain and the season of the year. Sufficient water should be present to cover the grain about five inches. The object of this operation is to prepare the seed for germination by expanding the fecula with moisture: it is known to be completed if the grain, when pressed between the thumb and fingers, sheds abroad its flour; if it remains entire in the husk, the steep must be prolonged. The grain is next laid in small heaps on a stone floor, and allowed to remain for some days. It presently becomes warm, and gives off moisture; the fibrillæ of the radicle soon appear, and at length the plumula, called the *acrospire* by the

maltsters, sprouts forth. The grain then becomes lighter coloured and more friable; the greater part of the gluten and a portion of the starch disappear, the latter having passed into the state of sugar; and the grain now contains a small quantity of diastase, derived from the transformation of some of the gluten. When the germination is considered to be sufficiently advanced, its farther progress is prevented by the application of artificial heat in the process called the kiln-drying. A layer of malt of three or four inches thick is spread on a perforated floor, either of tile or cast-iron, which is heated by a stove underneath, so that hot air passes up through the floor and malt. The temperature of the malt should at first be between 90° and 100° Fahr.; but when nearly dry it is raised to between 120° and 160° , and maintained at that heat until the requisite shade of colour is obtained. Malt is distributed into three sorts, according to the temperature at which it has been dried, pale, yellow, and brown; the pale malt has been exposed to the lowest degree of heat. In the operation of kiln-drying the principal object is to expel the moisture of the germinated seeds, and to put a stop to the germination; but it serves also to convert into dextrin a portion of the starch which remained unchanged into sugar, in the same manner as starch is converted into British gum by torrefaction. A small additional quantity of sugar is also formed during kiln-drying through the action of the diastase on the starch. In pale malt, however, these changes hardly happen; and hence, when examined by the microscope, most of the starch granules will be found unaltered.

The amount of diastase in malted barley scarcely exceeds one part in five hundred; but it is by the action of this small portion that the starch or the dextrin of the malt is converted into sugar in the first stage of brewing, that is, the mashing, preparatory to the fermentation. A solution of diastase has no remarkable influence on most vegetable principles; but on starch it seems to exert a specific action, converting it, as already remarked, first into dextrin, and afterwards into starch sugar. Liebig considers this property of diastase to depend on its undergoing spontaneous decomposition *in contact* with the starch, whereby the equilibrium of the molecules of the latter is disturbed through some process of induction, a new arrangement of the molecules taking place. The conversion of sugar into alcohol and carbonic acid by the vinous fermentation is referred to a similar cause, the decomposing substance in contact with the sugar being gluten or yeast. The change of starch into sugar, or rather, principally into dextrin, by the action of diastase, takes place on gelatinous starch even at the freezing point of water; but the conversion into sugar takes place most powerfully between 150° and 160° Fahr.: at the boiling point, diastase ceases to exert any influence on starch. So energetic is the action of diastase at the proper temperature, that one part in a state of active decomposition is said to be sufficient to saccharify two thousand parts of dry starch; but the larger the proportion of diastase, the quicker is the change.

It appears from the researches of Payen and Per-

soz, that starch may be converted by diastase, either into dextrin or sugar, according to the temperature of the mixture and the duration of the process. In a mixture of from six to ten parts of pale malt, one hundred of starch and four hundred of water, the starch is converted principally into dextrin at a temperature of 158° Fahr., continued for twenty minutes or half an hour; at a temperature of 167°, maintained for two or three hours, the starch is almost wholly converted into sugar.

In the common process of brewing, the mashing of the malt is commenced at a temperature of 150° Fahr. in summer, and at 167° in winter, and hot water is afterwards added in such a manner as to preserve a mean temperature of about 150° Fahr. At that temperature the conversion of the remaining starch into sugar is generally completed in an hour and a half, but the time depends on the quality of the malt. The liquor thus obtained, called the "wort," is then withdrawn, and another quantity of hot water added to the drained malt. The temperature of the second mashing should be between 167° and 174°. After the second infusion has been drawn off, the drained malt is frequently mixed with a third quantity of hot water, the wort thus procured being either added to that before obtained or else applied to fresh malt instead of water. Not being perfectly exhausted by the third mashing, the malt is sometimes mixed (after being again drained) with a fresh quantity of hot water, but this is not a common practice, as the residue of

the grains becomes thereby so impoverished as to be of very little value as food for cattle. The proportion of solid matter in solution in the third wort is generally about half as much as that in the second wort, and that in the second about half as much as that in the third. The quantity of water applied at each time is, of course, greatly varied according to the strength to be given to the beer. To make beer of middling quality, one quarter of malt requires to be mixed, at different times, with from one hundred and sixty to one hundred and eighty gallons of water, at 195° or 200°. The product of beer amounts to about two-thirds of this quantity. As soon as the wort is withdrawn from the grains, it is pumped into a copper to be boiled and hopped, and when cooled is mixed with yeast in order to excite the vinous fermentation of the sugar, that is, its resolution into alcohol and carbonic acid, but these parts of the process of brewing do not come under the subject of the present article.

It has been usual to consider as varieties of starch, two substances which have not yet been adverted to; namely, *inulin*, derived from the *inula helenium*, the *dahlia*, and some other plants; and *lichenin* or *lichen starch*, obtained from Iceland moss and other lichens. But both of these substances want the essential character of a true starch, that is, the ready production of a blue colour with iodine, as well as many other chemical and physical properties possessed by all the varieties of ordinary starch. Their composition, moreover, differs from that of starch. In-

ulin, by my analysis, is composed of $C_{24} H_{44} O_{11}$, and lichenin, by the analysis of Guerin Varry, of $C_{10} H_{11} O_{10}$.

To the physiologist starch is a highly interesting substance as an important element of food, not only of animals, but also, in one sense, of vegetables. "Its ready convertibility," observes M. Liebig, "without change of composition, into soluble forms, such as dextrin and sugar, adapts it admirably for carrying on those changes which occur in the juices of vegetables. It is stored up in the seeds, roots, and pith of plants, and by its decomposition furnishes the materials for many of the most essential vegetable products. It also serves as a most important element of the food of animals, furnishing not indeed the means of increase of mass, but the materials for keeping up respiration and supplying the animal heat. The fats and fixed oils of the vegetable as well as the animal kingdom are in all probability derived principally from the deoxidation of starch."

Formerly, starch was subject to a duty of three-pence farthing per pound, and its manufacture was consequently placed under the surveillance of the excise. Before being put into a stove to be dried, each paper of starch was sealed or stamped by the attendant officer, and the infringement of this regulation was attended with the infliction of a penalty on the manufacturer of one hundred pounds. The penalty for knowingly selling any kind of starch with a forged or counterfeit stamp, &c., was five

ndred pounds (Burn's Justice of the Peace, tit. arch).

The oppressive duty on starch, however, was abolished ten years since, in consequence of the recommendation of the Commissioners of Excise Inquiry. In the year ending 5th January, 1833, the nett produce of this duty amounted to a little more than eighty-five thousand pounds; the quantity of starch on which duty was levied being just eight million pounds.

TANNING.

§ I. On the properties of Tannic Acid and the astringent Vegetable Matters employed in Tanning.—II. Preparation of Hides and Skins for Tanning.—III. Modes of applying Tannic Acid to prepared Hides and Skins.—IV. Preparation of light and fancy Leathers.

THE conversion of the skins of animals into leather, which is the object of the process of tanning, consists in the production of a chemical combination of the skin with the astringent vegetable principle called *tannin* or *tannic acid*. If simply dried without being exposed to tannin or any substance which has the power of effecting a change in the nature of the skin, corresponding to that produced by tannin, the skin readily allows the percolation of water through its pores, is unable to resist continued friction without considerable abrasion, and speedily enters into a state of putrefaction if afterwards moistened. But each of these inconveniences may be surmounted by taking advantage of the property which skin possesses in common with some other animal tissues of forming a true chemical combination with tannin. If a piece of prepared skin* is placed in an aqueous solution of pure tannin, or in an infusion of some astringent vegetable substance containing tannin, as oak-bark or gall-nuts, and allowed to remain there for a short time, it separates the whole of the

* Skin which has been cleaned, soaked in lime-water, and freed from its extraneous appendages.

tannin from the liquid, and becomes hard, insoluble in water, almost impenetrable to water, and incapable of putrefying. By such a simple process as this, skin is converted into leather, but subsequent operations of dressing or currying are necessary to bring the leather into that state of pliability and complete impermeability to water which are essential in many of its applications. Similar, but less decided, changes may be produced in skins by impregnating them with a solution of alum or some other preparation of alumina, and also with oil or grease.

Processes for converting skin into leather have been practised in a rude manner from a very early period, and even among the most savage tribes; but it was not until towards the close of the last and the commencement of the present century that the principles of the processes were accurately developed through the researches of Deyeux, Seguin, Macbride, Proust, and Sir H. Davy; and tanners have in general been very tardy even to the present time in adopting the improvements suggested by the researches of these and other experimental philosophers. Until within the last few years, tanning has probably been more stationary than any other manufacturing process; but considerable modifications of the old method of tanning have been recently introduced, consisting chiefly in the employment of new materials. The result has not been, on the whole, an improvement in the quality of the leather, but a reduction in its price.

The leather manufacture of Great Britain is of very great importance, and ranks either third or fourth on the list; being inferior only in point of

value and extent to those of cotton, wool, and iron, if it be not superior to the latter (Mr. M'Culloch). Including the subsidiary trades of the currier, shoemaker, saddler, glover, &c., the manufacture of leather is considered by another authority to rank equal with, if not before, that of cotton.

The skin of animals is composed of two chief parts, the *corium* or *cutis*, and the *cuticle* or *epidermis*. The former, which is the true skin, is a tissue of delicate fibres crossing each other in all directions, more thickly woven towards the surface than in the deeper part of the skin. It is pervaded by a great number of little conical channels, the small extremities of which terminate at the external surface of the skin. These channels, which are placed obliquely, contain nerves, secretory vessels, and cellular membrane. The cuticle or exterior coating is an insensible horny membrane, composed of several layers of cells, devoid of blood-vessels.

A piece of fresh skin, freed on its internal side from fat and cellular tissue, and on its external side from the epidermis and the mucous membrane which lies between the epidermis and the true skin, contains about 43 per cent. of solid matter, the remainder being water. Of the solid matter, about 32 per cent. on the weight of the humid skin is the fibrous and cellular tissue and a little fatty matter, each of which is insoluble in cold water; 1·5 per cent. is uncoagulated albumen; about 1 per cent. is a variety of extractive matter, soluble in water and alcohol; and 7·5 per cent. is another kind of extractive matter soluble in water, but insoluble in

alcohol (M. Wienholt.) Nearly the whole of the albumen and other matters capable of being dissolved by cold water, may be separated by digesting the skin in that liquid. When the washed skin is dried and digested in ether, a small quantity of fatty matter is dissolved out.

By digestion in boiling water the greater part of the true skin becomes altered in properties, and dissolved; only some vascular and nervous filaments, with a little fat, remaining undissolved: and the solution, when slowly evaporated, leaves a residue of gelatin or glue. Gelatin does not exist ready formed in skin, but is produced by the action of boiling water. The term gelatinous tissue is conveniently used to designate all animal tissues which are convertible into gelatin by such a process. Dilute acids and alkalies possess the property of converting gelatinous tissues into gelatin even at the ordinary temperature.

Respecting the importance and extent of the leather manufacture of this country, Dr. Campbell makes the following striking remarks: "If we look abroad on the instruments of husbandry, on the implements used in most mechanic trades, on the structure of a multitude of engines and machines; or if we contemplate at home the necessary parts of our clothing—shoes, boots, and gloves,—or the furniture of our houses, the books on our shelves, the harness of our horses, and even the substance of our carriages,—what do we see but instances of human industry exerted upon leather? What an aptitude has this single material in a variety of circumstances for the relief of our necessities, and sup-

plying conveniences in every state and stage of life? Without it, or even without it in the plenty we have it, to what difficulties should we be exposed!" (Political State of Great Britain, vol. ii. p. 176.)

§ I. ON THE PROPERTIES OF TANNIC ACID AND THE
ASTRINGENT VEGETABLE MATTERS EMPLOYED IN
TANNING.

Although the astringent matter contained in several different vegetables is designated by the same name—tannin or tannic acid, yet all these bodies do not appear to be identical. The differences, however, which are perceptible in the properties of most of the substances which are thus classed together, are small, and seemingly of no great importance in the practical application of this vegetable principle, which forms the principal subject of the present article. Other astringent vegetable matters exist, the properties of which amply distinguish them from tannin.

The most characteristic properties of tannin are astringency in taste, and the power of being precipitated from its aqueous solution, either of a blueish-black or dark green colour,* by a solution of a salt

* The colour of the precipitate produced in a solution of tannin by persalts of iron has been made the basis of an arrangement of the different tannins into two varieties, distinguished as tannin which precipitates iron blueish-black, and tannin which precipitates iron green. The experiments of Berzelius, Geiger, Walzl, and Cavallius, would tend to prove that the tannin in all plants is essentially the same substance, the different colours of the various precipitates with persalts of iron depending on the accidental presence of impurities, and also on the nature of the salt of iron used. But the more recent researches of Dr.

of the peroxide of iron, and of a dirty white or brown colour by a solution of gelatin. The precipitate produced in a solution of a persalt of iron, which is the tannate of peroxide of iron, is the basis of common writing ink. A solution of proto-sulphate of iron (copperas), perfectly free from all peroxide of iron, experiences no immediate change on the addition of tannin; but the mixture instantly becomes deep blue or black on exposure to the air; through the absorption of oxygen and formation of the peroxide of iron. If cold aqueous solutions of tannin and animal gelatin (glue, bone-size, or isinglass,) are mixed in certain proportions, both of these bodies are almost completely thrown down as a precipitate, known by the name of *tanno-gelatin*, which generally contains about half its weight of tannin. Sometimes, particularly when heat is applied, or when the acid is in excess, the precipitate forms, on stirring, a very viscid and elastic mass, something resembling cascutchouc. In its chemical constitution tanno-gelatin is quite analogous to leather, and was at one time, in fact, generally regarded as that substance in a pure state. This cannot be the case, however; as gelatin does not exist

Stenhouse favours the conclusion that not only must the tannins of different plants which produce different coloured precipitates in the same solution of peroxide of iron be regarded as distinct substances, but even that some of the varieties of tannin which agree in their reactions upon salts of iron, and in their general chemical habitudes, are by no means identical. Dr. Stenhouse availed himself of a new test for tannin, which affords indications only with the variety of tannin contained in galls, and with gallic acid, which consists in the production of pyrogallie acid when the body to be tested is subjected to the destructive distillation. Pyrogallie acid is disengaged as a crystalline sublimate. (*Memoirs of the Chemical Society*, p. 132.)

ready formed in skin, and tanno-gelatin, unlike leather, is slightly soluble in water at the boiling point. The aqueous solution becomes turbid on cooling, owing to the reprecipitation of the tanno-gelatin. This compound may be also dissolved by an excess of solution of gelatin, but not by an excess of a cold solution of tannin. When dried, it loses its viscosity and elasticity, and becomes brittle and pulverulent.

Tannin may be most easily procured in a state of purity from gall-nuts, which are excrescences produced upon the tender shoots of certain species of oak, through punctures formed by a peculiar insect for the purpose of depositing her eggs. A quantity of coarsely powdered gall-nuts is placed in a glass percolator,* the bottom of which is plugged by a little clean cotton, and covered with common ether, which has previously been shaken with a little water. The percolator being fixed to its receiver and closed at top by its stopper, the mixture is allowed to digest for several hours; after which the stopper is removed, the liquid filtered into the vessel below, and the galls washed with more ether introduced at top.

On standing, the filtered liquid separates into two strata of unequal density: the lower, which is generally of an amber colour, is a solution of tannin in water; the upper is a solution in ether of some other substances contained in the galls, amongst

* The percolator or apparatus of displacement consists of a long and narrow vessel, open at both ends, contracted both at top and bottom, and fitted with an air-tight stopper at top: the bottom of this vessel fits into a matrass or bottle to serve as a recipient.

which is gallic acid. The aqueous solution when gently evaporated leaves a shining, porous, uncrytallised mass of tannin, nearly pure. By this process galls may be made to afford from 35 to 40 per cent. of their weight of tannin.

Tannin is very soluble in water, and its solution exhibits the usual properties of a free acid. When exposed to air, and particularly at a high temperature, the aqueous solution of tannin absorbs oxygen and disengages an equal volume of carbonic acid: the tannin wholly disappears, and in its place are found two new products, namely, gallic and ellagic acids; the former, being soluble, is contained in the liquid, but the latter is an insoluble powder of a yellowish-grey colour. In close vessels a solution of pure tannin may be preserved without change. Tannin is precipitated from a tolerably strong solution by sulphuric, muriatic, phosphoric, boracic, and arsenic acids; and these precipitates consist, according to Berzelius, of compounds of tannin with the acids respectively. If the compound with sulphuric acid is boiled for a few minutes in dilute sulphuric acid, the tannin becomes converted into gallic acid, which is deposited in coloured crystals as the liquid cools. When the sulphuric acid employed for this purpose is diluted with seven or eight times its bulk of water, the crystals of gallic acid thus obtained are colourless and nearly pure. An analogous change occurs where the compound of tannin and sulphuric acid is boiled with an excess of a caustic alkali (Liebig), and the action of muriatic acid on tannin is quite similar to that of sulphuric acid (Dr. Stenhouse). In these cases of the

conversion of tannin into gallic acid, the access of the air is unnecessary.

Gallic acid exists ready formed in several vegetables; among which are gall-nuts, sumach, the seeds of the mango-tree, divi, valonia, tea (black and green), and myrobalams. It is probably produced in all cases through the decomposition of tannin. Gallic acid is not nearly so soluble in cold water as tannin; but it is very soluble in hot water, and crystallizes on the cooling of such a solution in silky needles. When a solution of gallic acid is exposed to the air, it absorbs oxygen, becomes mouldy, and deposits a brown powder; but it may be preserved without change in a close vessel. In the appearance which it produces with solutions of salts of iron, gallic acid resembles tannin.* Gallic acid is of very little service in the process of tanning, being incapable of combining with gelatin and gelatinous tissue, like tannin. This fact must naturally suggest to the tanner the necessity of guarding against all the circumstances which favour the conversion of tannin into gallic acid, particularly where the vegetable matter employed is one of those which contains the same kind of tannin as exists in gall-nuts and sumach; since this variety is more susceptible of conversion into gallic acid than any other kind of tannin.

* With a solution of persulphate of iron, gallic acid produces a blueish-black precipitate, which gradually becomes almost colourless, owing to the reduction of the peroxide of iron to the state of protoxide. This does not happen when the original solution contains peroxide of iron, so as to form the ferroso-ferric oxide. Gallic acid produces no colour at first with pure protosulphate of iron, but the mixture soon becomes blue on exposure to the air.

From the recent researches of M. Wackenroder and M. Larocque, it appears that the formation of gallic acid from tannin is considerably expedited by the contact of the insoluble vegetable matters which remain after the extraction of the tannin; at least, in the case of nut-galls, and probably in that of all vegetable matters which contain tannin susceptible of this change by exposure to the air. M. Larocque found that all the tannin contained in an aqueous solution of that substance to which was added the residue of the preparation of tannin from gall-nuts, by means of ether (as described at page 167), became entirely converted into gallic acid, although in a closed vessel; while a strong solution of pure tannin freely exposed to the air during the same length of time contained nearly the whole of its tannin unaltered. It is hence concluded, that the insoluble residue of the nut-galls contains a substance capable of acting on tannin as a ferment, and that the change of tannin into gallic acid in such cases is a species of fermentation. This is rendered still more probable from the circumstance that the vinous fermentation may be excited in grape sugar by powdered nut-galls which have been digested in ether; and also that contact with yeast, blood, and albumen, produces the same effect on tannin as contact with the residue of nut-galls, though not with such rapidity as the latter. The gallic acid formed from the tannin of nut-galls through the agency of yeast is mixed with a quantity of a brown and bitter substance. M. Larocque has also observed that this fermentative decomposition of tannin may be prevented or retarded by all the antiseptic bodies which im-

pede vinous fermentation, as soluble salts of mercury, aromatic bodies, and empyreumatic oils. The presence of corrosive sublimate is said to prevent the decomposition almost perfectly. The access of the air is not essential to this transformation of tannin, according to M. Larocque, and no appreciable quantity of gas is disengaged during the action.

It has already been observed that dilute sulphuric and muriatic acids speedily effect the conversion of tannin into gallic acid without access of air, when the mixture is exposed to a moderate heat (page 168). According to the results of some recent experiments of M. Antoine, however, it appears that the decomposition of tannin by exposure to the air is not at all accelerated, but, on the contrary, rather retarded by the presence of a very minute quantity of either of these acids, provided the mixture is kept at common temperatures. Pyroligneous acid possesses the property of retarding the decomposition of tannin to a very considerable extent, probably owing in a great measure to the presence of certain empyreumatic bodies. On the contrary, tartaric and malic acids, and vegetable acids in general, accelerate the decomposition of tannin. The rapidity with which sumach ferments may be referred in a great degree to the presence of a considerable quantity of malic acid in the leaves, according to some recent analyses.

From the preceding observations may be inferred some of those conditions which the tanner should endeavour to avoid or obtain in order to retard as much as possible the conversion of the tanning principle into gallic acid, the latter being incapable of combining with gelatinous tissue. Though the

observations refer particularly to the tannin of gall-nuts, which is believed to be the same kind as that of sumach, yet there is every reason to believe that they are applicable to all vegetable substances which contain a variety of tannin; not even excepting those the tannin of which is not convertible into gallic acid; for all kinds of tannin are subject to a fermentative decomposition, though the different varieties may afford very different products, and in all probability, the same agents which possess the power of restraining the fermentation of one variety would that of another.

An idea prevails among some tanners, however, that gallic acid exerts some beneficial action or other in the process of tanning. This we may certainly admit, provided the ordinary process is followed; but undoubtedly it is at the expense of a far more valuable and important agent. That gallic acid is not absorbed by the skins, or at least not in any quantity, is obvious from its existence in very considerable proportion in the spent or waste tan-liquors, into which the prepared hides are introduced before they are put to digest in the stronger and more recent infusions. When hides which have been cleansed in the usual manner by means of lime-water, and not by means of sulphuric acid, are digested in the spent liquors, the gallic acid causes an expansion of the pores of the hides, which facilitates the penetration of the solution of tannin when the hide is transferred to the stronger liquors. This appears to be the only beneficial action exerted by gallic acid, and the same effect may be obtained by the application of almost any other acid. In

fact, sulphuric acid has long been economically employed for this very purpose.

The principal astringent vegetable matters now used as sources of tannin in the manufacture of leather are the following :

Oak-bark,	Cork-tree bark,
Valonia,	Mimosa or wattle-bark,
Light catechu or terra,	Birch-bark,
Divi-divi,	Myrobalams,
Sumach,	Larch-bark.
Dark catechu or cutch,	

The following materials were formerly employed to a small extent, but their use is now wholly discontinued in this country :

Willow-bark,	Elm-bark,
Oak saw-dust,	Bark of the Spanish chestnut.

Oak-bark. — In England, oak-bark has always been more extensively employed in tanning than any other substance. The bark is prepared for use by being simply ground to a coarse powder between two cast-iron cylinders. Bark cut in the spring contains a much larger proportion of tannin than that cut in the autumn, and that cut in the autumn more than that cut in the winter. The quantity of tannin in oak-bark is considered by all tanners to be in proportion to the freedom with which the sap was flowing at the time of stripping, and to the facility with which the bark is removed; hence that bark which presents the appearance of not having been easily detached, fetches a far lower price than that which seems to have been removed with facility. The richest bark is always obtained in the warmest

spring, as it then contains most sap; a few days only of cold weather previous to felling and stripping causes a very perceptible reduction in the proportion of tannin and sap. The bark of coppice-trees about twelve years old contains more tannin than that of younger trees, and the latter more than that of old trees.

According to Dr. Stenhouse, the tannin of oak-bark does not afford pyrogalllic acid when subjected to the destructive distillation, like the tannin of gall-nuts; from which circumstance it may be concluded that the tannin of the bark is not identical with that of galls. An analysis of oak-bark by M. Gerger afforded 5·6 per cent. of tannin; Sir H. Davy estimated the entire bark of middle-sized oak cut in the spring to contain 6·0 per cent. In this, and all other astringent barks, the tannin is contained solely in the inner white layers next to the alburnum; the middle coloured portion contains most of the extractive matter; and the epidermis, or exterior, contains little extractive matter and no tannin. According to common estimation, from three and a half to four pounds of oak-bark are required for the production of one pound of leather. The quality of leather made by means of oak-bark is considered to be superior to that of the leather made with either of the numerous tanning materials which are now so extensively employed in the place of bark. The process of tanning with bark, however, requires the longest time.

The present* price of English oak-bark is from five pounds to eight pounds per ton. The price of

* April, 1844.

foreign oak-bark (duty paid) per ton is as follows: Dutch from five pounds ten shillings to six pounds ten shillings; Flemish, from five pounds ten shillings to seven pounds ten shillings; and German, from four pounds to five pounds.

Sumach.—Sumach is chiefly used in tanning for preparing and finishing the lighter and finer kinds of leather, and is employed more extensively in dyeing and calico-printing than in tanning. It consists of the powder of the leaves and young branches* of the *Rhus cotinus* (Venus sumach, or the wild olive), *Rhus coriaria* (hide or elm-leaved sumach), shrubs which grow in various districts of the south of Europe. The *Rhus cotinus* is used most extensively in dyeing, and the *Rhus coriaria* in tanning. It is said that all the leather made in Turkey is tanned by means of the bark of the latter.

Sir H. Davy found a specimen of Malaga sumach to contain 16·4 per cent. of tannin, and one of Sicilian sumach 16·2 per cent. M. Cadet de Gassicourt obtained 10 per cent. of tannin from Virginian sumach, and five per cent. from sumach from Carolina. The tannin of sumach appears to be identical with that of galls; and gallic acid occurs ready formed in sumach to a considerable extent. When mixed with water, sumach is more apt to enter into a fermentative decomposition than any other tanning material.

The present price of Sicilian sumach is from nine pounds to ten pounds ten shillings per ton.

Divi-divi, or *divi*.—This astringent substance is

* The branches are probably added for the purpose of sophistication. Of late, to prevent this fraud, the sumach-leaves have been imported entire.

the pod of a leguminous shrub (*Cæsalpin coriaria*), a native of South America, which grows to the height of between twenty and thirty feet. Of late years it has been imported into Great Britain from the West Indies and various parts of the north coast of South America* in considerable quantity, and is become of general use among tanners throughout the country.

The pods are of a dark brown colour, about three inches in length, but curled up as if they had been strongly dried. The whole of the tannin resides in the rind of the pod, immediately underneath the epidermis; the taste of that part is highly astringent and bitter; but the inner skin, which encloses a few flat seeds, is nearly tasteless. Divi contains a considerable quantity of a variety of tannin which resembles that of galls in affording a deep blue or black precipitate with salts of the peroxide of iron, but differs from it in not producing pyrogallic acid on destructive distillation. Divi also contains a considerable amount of a mucilaginous substance, the presence of which interferes with the application of this article in dyeing and calico-printing, but not in tanning.

Divi, like sumach, soon enters into a state of fermentation when mixed with water. The leather made by means of divi is particularly porous; it is always coloured brown when the tanning is conducted in the ordinary manner, and frequently of a deep brownish-red. The circumstances which give rise to the production of the latter colour are not well

* It is principally exported from Maracaibo, Rio de la Hache, and Savanilla.

derstood. The colouring matter seems to be generated through a kind of fermentation in the infusion, which comes on suddenly both in cold and in warm weather, but more frequently in the latter; the leather and the sides of the tan-pit becoming covered with a purplish or blood-red deposit. If preserved out of contact with the atmosphere, the infusion does not afford this colouring matter, and the colour of the leather prepared in such circumstances is unobjectionable, being much better than could be obtained by applying the infusion in the ordinary manner, without the occurrence of the peculiar fermentation and production of red matter. Some tanners do not venture to expose their hides to more than two pits of infusion of divi, in order to prevent the attachment of much of the colouring matter. The buff-coloured deposit, technically known by the name of "bloom," is produced freely from an infusion of divi.

At present the price of divi is from nine pounds to thirteen pounds per ton.

Valonia.—*Valonia* consists of the acorn-cups of the *Quercus Ægilops* (prickly-cupped oak), a valuable tree which grows in abundance in the Morea and adjacent countries. About seven thousand five hundred tons of these acorn-cups are imported into this country yearly from Smyrna and the Morea, and sold almost wholly to tanners and dyers.

As soon as the cups are gathered, they are partially dried, and then conveyed on mules to Smyrna or some other port at which they are to be shipped, where they are stored up in warehouses for several months, being disposed in layers of from three to five feet in thickness. During this time the cups

undergo an incipient fermentation, and as they dry, the long spreading scales, which at first completely confined the acorn, become contracted and allow the acorn to fall out of the cup. When dry, the whole is picked over, to separate the damaged black cups, and all the acorns, which contain no tannin. The cups on the surface of the stratum always become damaged during the desiccation. The average diameter of the cups of common valonia, including the scales, is a little less than two inches. Another kind of valonia is met with in commerce, much smaller than common valonia, the average size of the cups being about that of a large cherry. This variety, which is distinguished by the prefix "Camata," bears a higher price than the other, partly from being a little richer in tannin, but chiefly from being in demand by silk-dyers. Camata valonia is said to be the fruit of a smaller species of *Quercus* than that which yields the common valonia; the acorns remain imbedded in the cups.

The quality of valonia may be ascertained by an experienced eye from the appearance of the cup, which, when good, is thick, full-grown, and of a bright colour. After being gathered, the cups are frequently exposed to heavy rain, whereby they become deprived of a great portion of their tannin, and darkened in colour. They are also frequently injured in the preparation for shipment.

The present price of valonia from Smyrna is from ten pounds to twenty-one pounds per ton: that brought from the Morea is less expensive, its price per ton being from eight pounds to fifteen pounds. About two pounds of valonia, on the average, are

required for the production of one pound of leather. It is said that the leather produced by means of valonia is harder and less permeable to water than that made with oak-bark, and so heavy as to constitute this the cheapest of all tanning materials, catechu or terra only excepted. The leather produced by a mixture of valonia and oak-bark is of very excellent quality.

The tannin of valonia appears to be different from that of nut-galls, as it affords no pyrogallic acid on destructive distillation. Dr. Stenhouse found only a trace of gallic acid in this tanning material. An infusion of valonia speedily affords the deposit of "bloom."

A considerable portion of last year's crop of valonia is said to be damaged by being covered with a substance resembling honey, which may act injuriously by undergoing a kind of fermentation when the valonia is shipped and put up in store.

Catechu.—The two astringent substances known by the names of catechu, cutch, terra japonica, and terra, are inspissated aqueous extracts made from the bark, wood, and probably leaves, of the *Acacia catechu*, and *Uncaria gambir*. According to Nees von Esenbeck, most of the catechu exported from Bombay is prepared from the former tree, and that exported from Bengal from the latter. Bombay catechu, which is the richest in tannin, is of a dark brownish-red colour, both externally and internally, and of specific gravity 1.38. This variety is commonly called *cutch*. The specific gravity of the Bengal catechu (terra), which is of a light brown colour internally, is only 1.28. The taste of both varieties is astringent and bitter, and after a time sweetish.

The process by which catechu is said to be prepared is the following. The tree having been felled, the whole is cut up into small pieces and boiled with water in a narrow-mouthed vessel until only one half of the original bulk of liquid remains. The solution is then transferred to a wide earthen vessel, in which the evaporation is continued; but the inspissation is completed by exposure to the sun, the mass being occasionally stirred. Before the extract becomes thoroughly dry, it is placed in cloths, strewn over with the ashes of cow-dung, cut into little lumps, and again exposed to the sun to be dried.

The appearance of the dark-coloured variety of catechu, or cutch, answers much better to this description of the mode of preparing catechu than that of the light-coloured variety. I have been informed that the latter, which is more pulverulent than the former, is prepared by mixing the concentrated decoction of the tree with a pulverulent substance resembling starch. This powder is disposed in a thin layer on a floor or shelf, and the concentrated infusion or decoction is allowed to run over the floor and be imbibed by the powder. When the mass is become stiff by drying, it is cut up into small lumps, which are placed before the sun to complete the desiccation.

Both kinds of catechu contain about half their weight of a variety of tannin different from that of galls, as it produces olive-green precipitates with salts of iron, and yields no pyrogallie acid on destructive distillation. The tannin of catechu is readily dissolved by cold water. Another peculiar principle exists in catechu, which has received the names of *cate-*

chin and *catechuic acid*; it is insoluble in cold water, but slightly soluble in the solution of the tannin of catechu. The light-coloured cubical variety of catechu did not afford Dr. Stenhouse any traces of gallic acid.

In India, catechu has long been extensively used in tanning, and of late years a considerable quantity has been consumed by the tanners of this country. Skins may be tanned with great rapidity by catechu, but the leather it produces is very permeable to water, light and spongy: its colour is dark reddish-fawn. The leather made by means of the light-coloured variety of catechu is softer than that made by cutch. An infusion of catechu scarcely affords any of the deposit of bloom which oak-bark, valonia, and divi yield. This is a material objection to the sole use of catechu as a tanning agent, since all purchasers of leather consider the existence of a coating of bloom to be an indication of the goodness of the leather. According to the experiments of Mr. Purkis, a given weight of catechu is capable of tanning as many skins as seven or eight times that weight of oak-bark; one-half that estimate, however, would probably be nearer the truth. A pound of catechu generally suffices for the production of about a pound of leather; and as the price of this article at present (April, 1844) is from thirteen pounds to fourteen pounds per ton, duty paid, it may be considered the cheapest of all tanning materials. A considerable quantity of this substance is used by calico-printers to produce a fast bronze on cotton fabrics.

Larch-bark.—The bark of the common larch-fir was formerly a very common substitute for oak-

bark in tanning, and it is still employed to a considerable extent in some parts of Scotland for tanning the inferior sheep-skins known by the name of "basils." It contains a large quantity of tannin, differing slightly from that of galls, but the quality of the leather made with it is inferior. Larch-bark also contains some resinous matter and a good deal of mucilage.

Myrobalams.—The astringent substance known by the name of myrobalams, which is the fruit of several East Indian trees, has long been employed in India as a substitute for galls. It has not yet been generally employed by tanners of this country; but from the large quantity of astringent matter which it contains, it probably deserves more attention than it has yet received. The ripe fruit is pear-shaped, weighing from seventy to one hundred grains, deeply wrinkled, and of a brownish-yellow colour. The husk, which is easily separated by bruising from the nut it encloses, contains the whole of the astringent matter, some mucilage, and a brownish-yellow colouring matter, which has been employed in India as a yellow dye. The tannin of myrobalams differs slightly from that of galls. The quantity of gallic acid in myrobalams is pretty considerable (Dr. Stenhouse).

Willow-bark.—The bark of the willow was occasionally employed in tanning, but to no great extent, as it produces little more than one third of the effect obtained by an equal weight of oak-bark. Its use is now almost, if not entirely, discontinued in this country. Sir H. Davy found the entire bark of the common willow to contain 2·3 per cent. of

tannin, and that of the Leicester willow 6·8 per cent. Danish leather, which possesses a peculiar and agreeable odour, and is much used for making gloves, is generally prepared from kid and lamb skin by means of willow-bark. Russia leather is also usually tanned with willow-bark, but the odour of that leather is due chiefly to the empyreumatic oil of the bark of the birch-tree.

Mimosa or wattle-bark.—This bark is obtained from different species of the mimosa which grow abundantly in Australia and New Zealand: a fluid extract from the bark was brought to England about twenty years since, and being approved of by tanners, small quantities of the bark and the extract have been regularly imported ever since. The leather made by means of this material is of excellent quality, but its colour is very objectionable. Unless very finely ground, mimosa-bark does not yield the whole of its tannin to warm water. This article has long been used in tanning in New South Wales. Its present price is from eight pounds to eleven pounds per ton.

Cork-tree bark.—The outer dead bark of the cork oak (an evergreen) is the substance commonly known as cork, which may be removed without any injury to the tree; but the inner bark, which is that employed in tanning, cannot be removed without producing the death of the tree. It is not commonly separated for commercial purposes, except in Corsica, Spain, and a few other countries, where the tree is indigenous and very abundant. It contains about twice as much tannin as oak-bark of average quality. This bark is used more extensively in Ireland than

in England. Its price is generally from eight pounds to twelve pounds per ton; but it has been much lower of late, owing to the increased importation of this article. The quantity imported into this country last year amounted to about ten thousand tons, and it is expected that eight thousand tons will be imported during the present year. Even the latter quantity is far above the average import.

The tannin of cork-tree bark appears to bear more resemblance in its properties to that of catechu than to the tannin of most other vegetable matters. Like catechu, cork-tree bark scarcely affords any of the light fawn-colour deposit called bloom, and it is doubtful whether this variety of tannin is susceptible of conversion into gallic acid. The dark colour which cork-tree bark always communicates to leather produced by its means, is the greatest objection to the use of this material.

Judging from the proportion of tannin found in some of these substances, Sir H. Davy determined their respective value to the tanner to be as follows; the relative quantities of dry hides capable of being tanned by equal weights of the materials, being expressed by the numbers.

Sumach	77
White interior cortical layers of oak-bark	72
Entire bark of Leicester willow, large size,	33
„ coppice oak	32
„ middle-sized oak, cut in spring,	29
„ oak, cut in autumn,	21
„ ash	16
„ Lombardy poplar	15
„ elm	13

Entire bark of common willow, large,	11
„ sycamore	11
„ beech	10
„ horse-chestnut	9
„ birch	8

If the tannin and all the other ingredients of these astringent matters were of precisely the same nature, such a table as the above might exactly indicate the respective value of the different substances. But the tanner has to take cognizance of other circumstances than the actual proportion of astringent matter contained in his material; for it is well known that a considerable difference may be detected in the quality of leather made from similar skins and in the same manner, but with different vegetable matters, though the leather be perfectly tanned: this can only be ascribed to a difference in the nature of the tannin, or the accompanying mucilaginous and other matters. The leather produced by means of larch-bark, for example, is far inferior to that made with oak-bark, though similar skins be operated on, and the tanning be continued the same length of time; and catechu and divi produce a more porous leather than oak-bark or valonia.

The quantity of colouring matter present in the tanning material, and the susceptibility of the latter to produce a soluble colouring matter on exposure to the air, form another important subject for the consideration of the tanner. The quality of the leather may not be in the least affected by the attachment of vegetable colouring matters; but the prejudice of purchasers requires that both upper and sole leather should possess an uniform dull fawn-

colour, or what is still preferred, a yellowish fawn-colour. The infusions of several of the tanning materials which have been recently introduced, either contain when first made, or afford on exposure to the air, dark reddish-brown colouring matters which become permanently attached to the leather. The slow conversion of tannin into gallic acid by exposure to the air is generally, and probably always, attended with the formation of a dark brown substance (the apothème of Berzelius) sufficiently soluble in water to colour the leather through its entire thickness. The principal objection to the use of the cork-tree bark consists in the presence of such a colouring matter as this in the infusion of the bark, particularly after it has been freely exposed to the air; and light catechu and cutch, though generally about twice the price of oak-bark, would be esteemed cheaper than any other tanning material were it not for the reddish-brown colour which they communicate to the leather. Although the recent infusions of all vegetable tanning materials contain more or less of this apothème, yet there can be no doubt that the quantity is greatly increased by a free exposure to the air: hence another reason, besides that alluded to at page 169, for protecting the pits as much as possible from all oxidating influences.

The only method of ascertaining the quantity of astringent matter in tan-liquors and tanning materials, now in common use among tanners, that of taste excepted, is by the application of the saccharometer or hydrometer to the liquor, or to an infusion made from a small weighed quantity of the material

for this express purpose, whereby an indication of the specific gravity of the liquor or infusion is obtained. This method, however, is inadequate, since the specific gravity of the liquor is increased not merely by the tannin, but by the colouring matter, which is in most cases an actual nuisance to the tanner, and by all the substances in solution, whether absorbable by the hide or not. The spent liquor, which contains no matters capable of combining with the hide, is always denser than water. The indications of the hydrometer may be of a little service, however, in ascertaining the strength of a liquor made from only one kind of tanning material, or even from a mixture of different materials always in the same proportions; the allowance which should be made for the matters in solution not absorbable by the animal fibre having been previously determined in a rough manner by the density of such a spent liquor as the infusion under examination would yield. But no dependence whatever should be placed on the hydrometer as a means of ascertaining the value of a new tanning material, or of the relative strength of tan-liquors made from different materials, unless the densities of the spent liquors are taken into consideration. The principal recommendation of the hydrometer is the facility with which that instrument may be applied.

Another method, more frequently practised by the chemist than by the tanner, is by determining the weight of the precipitate of tanno-gelatin (page 166) produced on mixing a solution of glue or isinglass with the tanning infusion. The results thus obtained are in general nearer the truth than the indications

of the hydrometer, but are far from being always worthy of confidence. The composition of tannogelatin varies greatly according to the manner in which the precipitate is produced. If made by mixing solutions of tannin of oak-bark and gelatin in such proportions that no great amount of either predominates, it generally consists, when dried at 212° , of 100 parts of gelatin, and about 88 parts of tannin; if made by adding a great excess of a strong solution of tannin to the solution of gelatin, it contains 100 parts of gelatin, and about 118 parts of tannin; but if made with an excess of gelatin, it contains 100 parts of gelatin, and about 60 parts of tannin.* It would be difficult to precipitate the whole of the tannin in this way without applying the gelatin in slight excess, but the precipitate at first formed would then partially redissolve in the excess of gelatin. Some varieties of tannin, moreover, produce much larger precipitates with gelatin than other kinds: infusions of cork-tree bark and cutch, for instance, afford smaller precipitates than an infusion of gall-nuts of similar strength; hence this test would be inapplicable to a tan-liquor made of mixed materials.

If the tannin to be estimated is the same kind as that which exists in gall-nuts, a solution of sulphate of quinine may be used as the precipitant much more advantageously than a solution of gelatin. According to M. Larocque, sulphate of quinine precipitates tannin from its solution perfectly, and the composition of the precipitate seems to be constant;

* It will be perceived that the proportions of tannin in the three precipitates are nearly as 1, $1\frac{1}{2}$, and 2, respectively.

but different kinds of tannin are also unequally affected by this agent. The test solution may be prepared by dissolving the sulphate of quinine of the shops in water acidulated with a few drops of sulphuric acid.

The most ready method of obtaining the strength of a tan-liquor, and the only accurate method which would be frequently practised in a tannery, is an imitation on the small scale of the actual process of tanning, which would afford not merely the proportion of tannin, but that of all the matters in the liquor capable of being absorbed by the hide. A piece of perfectly dry prepared hide or skin, such as the clippings used for making glue, is digested in a given quantity of the liquor, till all the tannin, &c., have been separated, then taken out, slightly washed, dried, and weighed. The increase on its weight is, of course, the weight of the tannin and other matters required. An experiment of this kind may be completed in a few hours if a thin skin be operated on, and the action be assisted by a moderate heat. Care should be taken to have a greater quantity of hide or skin present than is sufficient to combine with all the tannin in the infusion.

One principal respect in which the common modern processes of tanning differ from the process generally practised until towards the close of the last century, consists in the mode of preparing the infusion of the tanning material as well as of applying it to the prepared hides. Anciently the infusion was commonly made in the pits where the impregnation of the

hides was effected; the ground bark and hides being laid in alternate layers in the tan-pit, which was then filled with water to the brim. When the infusion appeared to be spent, the pit was emptied, and refilled with fresh bark and water; and this operation was repeated whenever the bark became exhausted. This tardy process is still practised to a small extent, and by it leather of superior quality is produced; but to obtain a more rapid impregnation of the hides, the tanning infusions are now almost always prepared at first in a much more concentrated state than they could be obtained when applied as in the old method. The use of the simple aqueous infusion of the tanning material was proposed about the close of the last century by M. Seguin, who recommended that the infusion should be prepared by passing cold water through a stratum of the powdered vegetable substance until the latter, by several successive infiltrations of the same quantity of water, becomes completely deprived of its ingredients, which are soluble in cold water. The manner of applying the infusion thus obtained to the hide will be considered in another section of the present article. A large number of tanners now make their tanning infusions with hot or lukewarm water; the usual source of heat being steam, which is introduced by a large iron pipe to the bottom of a deep rectangular pit containing the mixture of the vegetable material and water. At a little height above the true bottom of the pit is placed a perforated false bottom, through which the infusion filters into the space below, from whence it is withdrawn by a pump.

The following mode of preparing a strong tan-

liquor adapted to the production of leather, by the modern quick process, is found to work well. The water, instead of being mixed with the fresh tanning material, which we may suppose to be bark, is first applied to bark which has already been almost exhausted of its soluble ingredients, and after the mixture has digested a considerable time at a moderate heat, the weak infusion thus obtained is pumped into another pit containing more bark, not so far exhausted as that in the first pit. From the second pit, after a time, the infusion is transferred to another containing richer bark; and so on, through a series of several pits, until it arrives in that which contains the fresh material. From the latter the liquor is withdrawn for use.

§ II. PREPARATION OF HIDES AND SKINS FOR TANNING.

In commercial language, all kinds of skins which are operated on by the tanner are arranged into three classes, technically known as hides, kips, and skins. *Hides* are the skins of large and full-grown animals, such as oxen, cows, horses, bulls, and buffaloes; *kips* are the skins of the same animals flayed while young;* the name *skins* is applied by the tanner to those of small animals, as sheep, seals, goats, dogs, &c. Hides are used for making thick and strong sole leather, and kips and skins for the

* Most of the kips which are imported, however, are the skins of full-grown, and often very old animals belonging to a small breed of cattle. This remark applies to those exported from Russia as well as from the East Indies.

The skin of a calf which has been out at grass is termed a kip; but if the animal has not been taken to grass, it is considered a skin.

thinner and more flexible upper shoe-leather, glove and fancy leather, &c. Hides, kips, and skins may be obtained by the tanner in four different conditions; fresh from recently slaughtered animals, dried, salted, and both dried and salted: the fresh hides are furnished by the home slaughter, the others are imported. Some idea of the relative estimation in which equal weights of the different kinds of hides are held by the British tanner may be formed from the following list, arranged in the order of their value, beginning with those most esteemed:

Dry ox and cow hides from Buenos Ayres and Monte Video.		
Dry	„	from Valparaiso.
„	„	from Rio Grande.
„	„	from the West Indies.
Dry salted	„	from Brazil.
Salted	„	from Brazil.
Salted ox hides from Buenos Ayres and Monte Video.		
Salted cow hides from Buenos Ayres and Monte Video.		
„	ox and cow hides	from New York.
„	„	from New South Wales.
Market or fresh hides.		

The highest price of the best Monte Video hides (dry) is generally eightpence per pound (duty paid), and the lowest price current of the worst hides from New South Wales (salted) is twopence halfpenny per pound. Kips are imported from the East Indies, dry, brined and dry salted; from Buenos Ayres, salted; and from St. Petersburg, dry. Their prices vary from fourpence to one shilling per pound. Sheepskins are mostly imported from Buenos Ayres, and seal-skins from Newfoundland.

The price of market hides varies from twopence halfpenny, to fourpence per pound. Though the lowest in price, they are considered the most valu-

able, and are the most expensive, owing to the large quantity of water present in the pores. To produce forty pounds of leather, there are required, on the average, thirty pounds of dry hide, sixty pounds of salted hide, and seventy-four pounds of market hide. The horns in the latter weigh, on the average, about eight pounds.

All kinds of hides and skins have to be submitted to certain preliminary operations before they are subjected to the action of the tanning agent; the principal objects of which are the removal of any small portions of flesh or fatty matter which may adhere to the cutis from imperfect flaying, the removal of the hair, epidermis, and dirt, and the distension of the pores of the hides and skins, whereby they are rendered more susceptible of the action of the tanning principle.

As the processes for preparing hides for tanning differ in some respects from those for preparing skins, it will be convenient to consider these operations separately; and the modes of preparing hides may be first noticed. In the manufacture of the same kind of leather almost endless variations may be discovered in the minute details of the processes practised by different tanners, a description of only the leading features of which can be included in the limited plan of the present article.

1. *Preparation of hides.*—The first operations to which dried hides are submitted are a thorough soaking in water, and repeated rubbing and beating, or treading under feet, in order to soften

and bring them as near as possible to the fresh state. The beating is now commonly executed by a machine quite similar to the fulling-mill of the woolen manufacture, in which the hides are exposed to the long-continued action of two heavy wooden mallets or stocks.

When fresh or "green" hides are to be operated on, a long preliminary soaking in water is not essential: such hides, after having had their horns removed, are simply washed in water in order to clear them of the blood and filth they may have collected at the slaughter-house, and are then sometimes scraped with a knife on the flesh side, to remove any small adherent portions of flesh or fatty matter; but the scraping is generally performed at a subsequent part of the process. Salted hides are also occasionally scraped when in this stage, but dried hides are not. This scraping is executed on a wooden or stone horse, called the beam (see fig. 29). The subsequent treatment of all kinds of hides is the same.

The next process to which the hides are submitted has for its principal object the removal of the hair. Several different methods of accomplishing this object have been practised; the oldest of which and that most extensively followed, both in Europe and in America, consists in the application of a solution of lime. The vessels in which the hides are impregnated with the solution of lime are stone or brick-built cisterns, sunk in the ground. Several of these pits, containing lime-water, or very weak milk of lime, of three or four different strengths, are arranged together in a series. The softened and washed hides

are introduced first into the weakest lime-pits, and after having remained there for a day or two, are transferred to the next in gradation, and so on, until the hair and epidermis readily yield to the touch, and the hides present certain appearances indicative of a sufficient action of the lime. During the whole of this process it is usual to "handle" the hides about once a day in order to equalize the action. This process of handling merely consists in taking the hides up out of the pits and allowing them to drain in a heap for an hour or two, after which they are returned to the pits. It is a common practice to stir the liquid immediately before the introduction of the hides, so that each hide may be in contact with some solid particles of lime.

The time requisite for the liming of hides varies from one to three weeks, and for the skins of sheep from two to five days; it being dependent on the texture of the hides and the state of the atmosphere. Lime-water does not continue the action a sufficient length of time without a frequent renewal of the solution; hence it is always usual to have a little more lime present than the water is capable of dissolving at once. It was formerly the practice of some tanners to take the hides out of the lime-pits after a few days' immersion, and pile them in a heap on the ground: having remained in this state for about a week, they were returned to the same pits from whence they were taken, and after a short time again taken out and drained; these operations were repeated until the hair and epidermis could be easily scraped off.

When taken out of lime-pits, the hides are laid

singly upon an arched wooden or stone bench, called the "beam," one end of which is raised, as shewn in the annexed figure. With the assistance

Fig. 29.



of a curved two-handled iron scraper, called the unhairing knife, the beams-man then removes the loosened epidermis* and hair; and afterwards with a similar but sharper instrument, called the fleshing knife, he removes the flesh and fat adhering to the other side, unless they had been separated before the hide was limed. After another slight scraping and a thorough washing in water, in order to withdraw as much of the lime as possible, the hides are ready to be exposed to the tanning infusions.

In some other methods of unhairing the hides, the softening of the epidermis and the roots of the

* The epidermis is incapable of combining with tannin and forming leather; the basis of this membrane being horny matter, and not gelatinous tissue. If the epidermis is allowed to remain on the hide, the tan-liquor would penetrate only through the flesh side, and the process of tanning would thereby be considerably lengthened.

hair is effected by the production of an incipient fermentation or putrefaction. With this view the hides, after having been laid in a heap for two or three days, are sometimes suspended in a close room, called the smoke-house, heated a little above the ordinary temperature by a smouldering fire fed with spent tan, which does not burn with flame. In a similar process, sometimes pursued in Germany, the hides are laid in a heap and covered with spent tan or some other imperfect conductor of heat, to confine the heat generated by the fermentative decomposition of the roots of the hair and other constituents of the hides. This process is attended with considerable risk, and is nowhere extensively adopted. In another process of the same nature, the hides are piled upon a bed of litter and covered with the same material for twenty-four hours. At the expiration of this period they are turned over, and are afterwards frequently examined to ascertain when this part of the process is complete. The process of liming, though objectionable, is far superior to either of these fermentative processes, as the quantity of gelatinous tissue which is lost in the latter is generally much greater than that lost in the former.

The processes in which the softening of the epidermis and roots of the hair is effected by an incipient putrefaction are practised much more extensively on the Continent than in Great Britain. In the Parisian tanneries it is common to impregnate the hides which are to be subjected to these processes with a small quantity of salt, not sufficient to prevent the decomposition and disintegration of

the roots of the hair, but enough to retard the putrefaction of the gelatinous tissue.

The softening of the epidermis and roots of the hair may also be effected by means of acids, applied to the hides in a state of a dilute aqueous solution. With this view, sulphuric acid, sour milk, pyroligneous acid, fermented barley and rye water, and a few other vegetable acidulous matters, have long been employed, the process of liming being then altogether dispensed with. The acid liquid obtained by exciting the acetous fermentation in a mixture of barley or rye flour and water, was extensively employed on the Continent at one time in the place of lime; and this same liquid is still sometimes applied for the purpose of swelling the hides after the removal of the hair by means of lime. An acid liquid prepared by digesting spent bark in a little water for six months, or until the liquid became as acid as ordinary vinegar, was also used in some countries as another substitute for lime.

Besides facilitating the detachment of the epidermis and hair, all diluted acids possess the power of swelling the pores of the hide to a very considerable extent, thereby enabling the tanning liquid to penetrate readily through the substance of the hide in the next part of the process. The hides also become swollen by the ordinary process of liming, but not to such an extent as when acids are applied; and it is a common practice among some tanners to swell the hides, by means of an acid, after they have been cleansed and unhaired by lime in the usual manner. Sulphuric has been the only acid employed for this purpose for some time past, but

formerly various vegetable acidulous matters were used for the same purpose.

The solution of sulphuric acid employed for swelling, or, as it is termed, "raising" the hides, may be made by mixing about one part of oil of vitriol with one thousand of water; but the acid may be used of different strengths, and the hides be transferred from a weaker liquor into a stronger until they are properly raised. By maintaining the liquor at a moderate heat, the hides may be sufficiently swelled in less than twenty-four hours. The leather prepared in this way is of excellent quality, and fetches a higher price than similar leather, in the preparation of which the swelling with sulphuric acid is omitted. Oxalic and tartaric acids possess the power of swelling hides to a greater extent than sulphuric acid, but the expense of these acids precludes their application in this process on the large scale. The use of sulphuric acid was proposed by Macbride in 1774.

Of all the means of facilitating the removal of the epidermis and hair which have been alluded to, the most common is the old liming process; but this method is not free from some important objections. That a considerable portion of the gelatinous tissue of the hide is disintegrated and decomposed during the liming process, being either removed from the hide in the form of soluble gelatin, or else so altered as to be rendered incapable of combining with tannin, can hardly be doubted, when we consider the energetic action which free lime exerts on organic bodies in general, and especially on animal tissues.

It is admitted by tanners that pelt which has been "high-limed" does not afford so heavy a leather as that which has been "low-limed," comparing the weights of the dry hides before being limed; and that the leather made from high-limed pelt is loose, and wears out quickly. Could every part of the gelatinous tissue originally contained in the hide be made to combine with a full proportion of tannin, then one hundred parts of perfectly dry hide freed from all extraneous appendages should form, when tanned by means of oak-bark, at least one hundred and seventy, or one hundred and eighty parts of leather: the increase in weight, however, depends in some measure on the strength of the tan-liquor, and also on the kind of tanning material employed, for a smaller quantity of some varieties of tannin suffices to tan perfectly, than of others. But the weight of the tannin and other matters absorbed by the hide from the tanning infusion, when the usual process is followed, rarely exceeds fifty parts on one hundred of the dry hide; and the increase in weight is still less when the unhairing and cleansing are assisted by exciting an incipient putrefaction by one of the processes already described (page 197). In a tanning process which has been of late practised to a very large extent in North America, in which the softening of the epidermis and the roots of the hair is effected merely by the application of cold water, the increase through tanning is said to amount to from fifty to eighty parts on one hundred of the dry hide. This considerable increase in the quantity of tannin and other matters absorbed by the hide, compared with the quantity absorbed when

the liming process is followed, is referred wholly to the circumstance that very little or no decomposition or alteration of the gelatinous tissue takes place during the unhairing and cleansing. The leather made by exposing to the tan-liquors pelt with its pores saturated with lime-water, is also decidedly inferior in quality to that made with the same kind of materials in a similar manner, with the exception of the pelt being freed from the lime as far as possible by washing and squeezing, before it is introduced into the weakest tan-liquor. The colour of the former leather is also darker than that of the latter.*

The American process of unhairing and cleansing, above alluded to, which is said to be followed almost universally in the large tanneries of New York, Maine, and New Hampshire, and to be continued wherever once adopted, is thus described in an article in the Journal of the Franklin Institute.†

“First, a vault or pit should be prepared for the reception of the hides, which, for convenience sake, should be twelve feet long, twelve feet deep, and ten feet wide. The walls may be built of stone, or a frame and planked. There should be an alley or vestibule for entrance not less than six feet long, having a door at each end; the outer one being made double, and filled in with tan, to prevent the communication of warm dry air from without. A ventiduct, made of plank, ten or twelve inches square, should extend from the centre of the bottom of the

* When pelt saturated with lime is soaked in the tan-pits, it presently becomes almost black, but the greater part of the colour disappears as the combination of the gelatinous tissue with tannin proceeds.

† For February, 1843.

vaults, three or four rods therefrom, and placed not less than four feet below the surface of the ground. This serves both as a drain for discharging the water of the vault, and to admit damp cool air, to supply the place of that which has become rarefied, and thus keep up a current through the ventilator at top. The ridge of the roof may be level with the surface of the ground : on the ridge, and extending its whole length, set up two planks edgeways, two inches apart. The space between these is to be left open, but cover the remainder of the roof with earth to the depth of not less than three feet. The covering of earth upon the vault and drain is to preserve a low temperature for the hides, so that they may unhair without tainting. Spring-water should be conducted, either in pipes or logs, around the angles formed by the ceiling with the walls of the vault; from which water should be allowed to flow in small quantities, either forming a spray, or falling so as to raise a mist or vapour, and saturate the atmosphere of the vault. The temperature of spring-water is generally about 50° Fahr. As water evaporates at all temperatures, it is plain that, if a constant supply be afforded, this evaporation, by requiring a large portion of heat, would keep the temperature of the vault nearly uniform. To suspend the hides in the pit, place three bars lengthways, at equal distances, near the ceiling, with iron hooks two or three inches apart inserted therein. Soak the hides as usual for breaking, then hang them singly upon the hooks by the butt, spreading them fully open. In the course of a few days, when the hair begins to loosen upon the upper parts, take

them down, raise the middle bar, and hang them by the other end until they will easily unhair. The hides should not be broken until they are taken from the vault, and ready to unhair. In a good vault, where the thermometer ranges from 44° to 56° Fahr., which it should never exceed, and where there is a free circulation of *damp* air, hides generally require, for unhairing, from six to twelve days. When the temperature falls below 44°, the ventilator should be partially closed; and when it rises above 56°, *cold damp* air must be forced in, or an increased quantity of cold spring-water may be thrown from a hose or otherwise."

The loosening of the epidermis and the roots of the hair in this process is considered not to be the result of any putrefactive decomposition of a portion of the hide, but to be produced merely by the softening action of the moisture, and this action seems to be confined to the surface or grain of the skin. But the temperature at which the operation is conducted is not low enough to prevent the occurrence of a very slight putrefaction, sufficient to disintegrate the roots of the hair, though probably not active enough to affect the gelatinous tissue. Against this idea it is urged, that no ammonia or other product of the putrefactive decomposition of animal bodies can be perceived in the vault; but the traces of these substances, which would be formed, might be completely dissolved and washed away by the constant stream of water. This question is of very little importance, however, if the gelatinous tissue remains unacted on, as is stated by those who follow the process. The loosening of the roots of the hair is

always the *first* effect of a putrefactive decomposition of the hide; hence purchasers estimate the soundness of hides by the force requisite to pull out the hair.

2. *Preparation of kips and skins.* — In this country, kips and skins are commonly cleansed and unhaired in much the same manner as hides; being first subjected, for about a fortnight, to the action of lime-water, or milk of lime of two or three different strengths, and afterwards scraped with the unhairing and fleshing knives. But particular care is required in the preparation of skins, to extract the whole of the lime which has been absorbed previous to subjecting the skins to the action of the tanning liquor. Lime, if allowed to remain in the skin in the unneutralized state, would tend to harden the leather considerably; but upper shoe-leather, and other light leathers, which are always made from kips and skins, should be quite soft and flexible: hence arises the necessity for carefully removing the lime by the process called “graining.” For this purpose, the kips and skins after having been limed and scraped, are commonly immersed in an alkaline lixivium, called the “bate” or “grainer,” made of the dung of hens, pigeons, and other domestic birds, in which they remain from eight to ten days, according to the temperature of the liquid. During this period they are frequently stirred about, and are occasionally scraped upon the beam, either on both sides or only on one side. Ten or twelve gallons of the dung are sufficient for a pit capable of “bating” one hundred skins.

By these operations the skins become rendered soft and pliant, the lime having been almost completely separated. Formerly the skins were withdrawn from the lixivium daily, and laid up in heaps to drain for half an hour. The process of bating then generally required nearly a fortnight.

It seems probable that, so far as the removal of the lime from the skins is concerned, the most active constituent of the bate is muriate of ammonia (sal-ammoniac), an aqueous solution of which would dissolve unneutralized lime, with the formation of chloride of calcium and free ammonia. A great inconvenience which attends the use of the common bate (the *fresh* dung) consists in the destruction of a portion of the gelatinous tissue of the skin by a fermentation excited through the decomposition of the animal matters of the bate. In warm weather, the grain side of the skin often becomes seriously coloured from this cause, when the process is not properly attended to. The flesh side, however, is first affected, but that is not of so much importance as the grain side. It is probable that a purer material than the bate in common use might generally be employed with advantage, particularly in summer. The use of the carbonate of ammonia as a bate, with other improvements in the process of tanning, some of which are elsewhere alluded to in the present article, was made the subject of a patent by Mr. Robert Warington, in 1841. Carbonate of ammonia does not dissolve the lime out of the skin, but destroys its causticity, by converting it into the carbonate, or chalk.

If the fresh bate is allowed to stand exposed to

the air for a few days before being used, it is much less disposed to act injuriously on the skin. Guano, which is the decomposing excrement of aquatic birds, has not the same action as the excrement of domestic birds.

Sheep-skins, before being soaked in milk of lime, for the purpose of being unhaired, should be squeezed in order to express as much as possible of the oil they contain. Bran-water is generally used as the bate in the preparation of sheep-skins. Seal-skins, which, when converted into leather, are principally used for the bindings of shoes, are well scraped, previous to being limed, for the same purpose.

Before the hides and skins are exposed to the tanning liquor, they are cut to a tolerably regular form by paring off their edges, and the clippings thus obtained are employed in the preparation of glue and size.

§ III. MODES OF APPLYING TANNIN TO PREPARED HIDES AND SKINS.

It is generally admitted that the quality of the leather made by the old slow tanning processes is decidedly superior to that of the leather made by the quick process now commonly practised by the tanners of this country, which differs from the old methods principally in the manner in which the tannin is applied to the prepared hides and skins. In one of the old processes, the hides, instead of being digested in an infusion of oak-bark, were merely placed

in contact with the powdered bark, the latter being slightly humid. A layer of spent bark, of about six inches in thickness, was first placed at the bottom of the tan-pit, the construction of which was just the same as that of those now used; and upon this substratum was placed a layer of about one inch in thickness of finely ground fresh bark. Over this layer a hide was carefully placed, so as to lie quite flat, and upon the hide another layer of fresh bark, which was surmounted by a hide and a layer of bark alternately, until the pit was completely filled. The whole was then covered by a stratum of six inches of bark, called the "hat," and compressed by being well-trodden under the feet. At the expiration of about two or three months, by which time the tannin of the bark had become united with the animal fibre, the pit was completely emptied of its contents; and the hides, after being stretched, were again disposed in the pit, with a fresh quantity of bark, in a similar manner. This process was again repeated three or four months later; and when the bark was supposed to be spent, and the leather almost fully tanned, the pit was commonly nearly filled with a strong infusion of bark, which served to complete the process.

As tannin can penetrate the hide only in a state of solution, it is obvious that the process just described must have been extremely slow, for the only liquid present to dissolve the tannin was the water in the hides, and the hygrometric moisture of the bark. It was usual in some places, however, to introduce to the bottom of the pit a little clean water,

the vapour of which served to accelerate the absorption of the tannin to a small extent, by becoming condensed on the bark and hides.

In the most common of the old tanning processes followed in this country, the tan-pit was filled to the brim with soft water, the hides and layers of bark having been first disposed in the manner above described. In the course of two or three months the pit was emptied and refilled as before, and this operation was repeated whenever the bark appeared to be spent. At the last filling of the pit, an infusion of bark was sometimes used in the place of fresh water. This process is not yet entirely abandoned, and the quality of the leather it affords is superior. The average time required for tanning a hide of moderate thickness in this way is two years.

In a similar mode of tanning, which is still practised, but may now be classed among the old processes, an infusion of bark is used from the beginning to the end of the operation, in the place of clean water. The hides and layers of bark are arranged as above described. The combination of the tannin with the animal fibre is thereby effected more rapidly than by either of the preceding methods.

Since the close of last century, the mode of tanning by means of an infusion of the tanning material has gradually come to be adopted, either partially or entirely, in every extensive tannery in the country. In this process, the prepared hides and skins are always first introduced into an infusion which has been almost perfectly exhausted of its tannin, and are afterwards subjected to the progressive action of

several stronger infusions, until they become perfectly tanned, no white streak appearing in the middle of the section of the hide or skin. The infusions are generally arranged by the tanner into two kinds, according to their strength, namely, "handlers," and "layers" or "bloomers." The actual tanning of the hides and skins may be completed in a short time in the handlers; the layers or bloomers, which are the strongest, being generally intended only to produce the deposit of "bloom."

In the details of this process, considerable differences may be found in the practice of different tanners, and also in the preparation of different kinds of leather. These relate not only to the kind of tanning material employed, but to the mode of preparing the infusion (some using cold water for this purpose, others hot water, and others the exhausted liquor or other weak infusion*), to the strength of the infusion, and to the manner in which the hides are laid in the pits. Some tanners place the hides in horizontal layers, others suspend them vertically, and others sew the skins up in the form of bags, which are filled with tan-liquor and immersed in the pit. The last method, which is known as the Danish, answers well for light skins, and is always followed in the tanning of the skins of sheep; but the great space it requires must prevent its general adoption in the tanning of hides on an extensive scale. The most common method of disposing the hides is in horizontal layers.

In some tanneries, the tanning of the hides is

* Some observations on the mode of preparing the infusions have already been made in another section of this article (page 190).

completed by an infusion only: but the most common practice is to use the infusion alone only in the handlers, and in the bloomers or layers to introduce some of the ground fresh material with a recent infusion. Some tanners introduce a very little ground bark in the two or three strongest handlers, and use the simple infusion only in the weaker pits. If the process is to be completed by an infusion alone, the hides may be "handled" (that is, taken out of the pit and again introduced either into the same or another) once or twice a day when in the spent infusions, every second day when in the stronger handlers, and once a week when in the bloomers. In handling, the usual practice is to take out the hides by one at a time, and lay them doubled in a heap on a sloping wooden rack placed over one half of the pit, and after allowing them to drain for one or two hours, to return them to a liquor, the last hide taken out being the first returned. While they are thus lying in a heap, the pressure of the upper hides tends to force the spent liquor from the pores of the lower ones, and therefore, we may suppose, to render the latter more absorbent of the liquor into which they are next introduced. It is believed, however, by some intelligent tanners, that any advantage which might be derived by allowing the hides to remain in a heap is more than counterbalanced by some other action, which tends to injure the quality of the leather, and that if the hides and skins are transferred immediately from one pit into another, the leather they afford is much firmer, tougher, and has a better texture, than if they are allowed to drain in a heap. It is not improbable

that the free access of air, in the latter case, may be attended with some injurious effect.

When the hides are "raised" by being soaked in dilute sulphuric acid, after having been unhaired and cleansed by the usual liming process, it is common to tan them from the beginning by means of the mixture of the fresh tanning material and an infusion, instead of the infusion alone. This is the most common mode of tanning hides pursued in Scotland, and the leather thus prepared is distinguished by the name of "backs," or "vitriol backs." The tanning of skins intended for upper-leather is sometimes begun and completed by the infusion, but it is usually begun in the handlers and completed in the layers.

A mode of tanning has been proposed and patented by Mr. Osmond Cagwell, an American tanner, a modification of which might probably be adopted with advantage in the commencement of the tanning of skins. In this process the hides or skins are laid upon layers of sawdust or other soft porous material, contained in shallow rectangular boxes, of which any required number may be arranged in a series, one box being placed about a foot over the next below it. The edges of the hides are raised a little so as to make of each hide a shallow trough, into which the tanning infusion is admitted. As the liquid becomes exhausted of its tannin and filters through the hide and sawdust, it is allowed to pass off through a channel leading from the bottom of the box, and the hide is at the same time replenished with a fresh liquor. It is said that the tanning may be effected very expeditiously in this way, but

it is necessary to immerse the hides in the tan-pits in the ordinary manner for three weeks or a month, in order to complete the tanning of the raised edges.

This process would seem better adapted to commence than to complete the tanning of hides, as the percolation of the tan-liquor must become retarded as the combination of tannin with the hide progresses. The necessity for completing the tanning of the raised edges by the usual method is not considered an important objection to this process by tanners. The edges of a hide are much more easily tanned than the body, and an objection raised by many purchasers of leather to the modern quick processes is the over-tanning of the edges of leather thus prepared. The circumstance that in the above process no labour is required for the purpose of handling the hides while being tanned, would materially contribute to the practicability of this mode of tanning on an extensive scale, at least in this country.

In a successful process contrived specially for the purpose of avoiding the labour of handling, the hides are fastened at one of their edges to a horizontal wooden frame, from which they are allowed to hang vertically in the tan-liquor. The frame being suspended by pulleys and a rope, all the hides may be lowered and raised at once.

The facility with which hides become tanned is considerably affected by the presence of unctuous matters in the hide; those parts which abound most in oils and fats being acted on with the greatest difficulty. An unequal distribution of fat, in fact, is one of the principal causes of the inequalities sometimes perceived in the same piece of leather. During

the liming process, a portion, but not the whole, of the fat in the hide combines with lime and becomes thereby converted into an insoluble soap, which is inert, so far as the tanning infusion is concerned.

As soon as the leather is taken out of the last blooming-pit, or layer, it is slightly washed in cold water; a thorough washing is avoided, lest any portion of the bloom on the surface of the leather should be removed in this operation. After being allowed to drain, the leather is dried in a room at a moderate temperature, which may be heated, in winter, by the circulation of steam in pipes, but artificial heat should be applied only in very cold weather. The leather may be suspended on poles.

Before it is thoroughly dried, the leather is subjected to a mechanical operation intended for the production of a smooth surface. In some tanneries, this merely consists in drawing a brass roller, about six or seven inches in diameter, over the grain side, the leather being laid flat on the floor. In other establishments, the leather, before being thus rolled, is "struck," or scraped with an iron instrument in the shape of either a three or four sided prism, furnished with a handle at each end, the leather being laid upon a sloping bench: this operation is very similar to that of "beaming" (fig. 29, page 196). Sometimes, instead of being struck or rolled, the leather is hammered upon a block, and occasionally it is hammered after being both struck and rolled. The "vitriol backs" prepared in Scotland are always hammered. After being thus treated, the leather is

returned to the drying-room, to be rendered completely dry.

Frequent allusion has been made in the course of this article to the yellowish-fawn coloured deposit from the tan-liquors, called the bloom, which is found not merely on the surface of the leather, but at a minute depth beneath.* The existence of this deposit is almost essential to the sale of the leather, although it is subsequently removed by the operations of the shoemaker or currier, and forms a useless addition to the weight of the leather. It is not mere prejudice, however, on the part of the purchaser, that requires the tanner to allow the bloom to remain upon the surface of the leather. It is almost universally admitted that the quality of leather made by the modern quick processes and by means of the tanning materials which have been so extensively introduced of late years, is inferior to that of leather made by the old slow processes, and by means of oak-bark. Now it happens that a good, healthy deposit of bloom is not easily obtained unless considerable time be allowed for the tanning; and while most of the new tanning materials produce a bloom differing in appearance from that produced by means of oak-bark, some of them yield hardly any bloom at all. For these reasons most purchasers of leather consider the presence of a good bloom to be an evidence of the goodness of the leather. Some observations on the blooming powers of different tan-

* It is confidently affirmed by some tanners that small solid particles may be absorbed into the substance of the hide in the process of tanning: if so, there is no mystery in the presence of bloom beneath the surface of the leather.

ning materials have already been offered in a previous section.

The nature and composition of bloom are involved in some uncertainty. The circumstances of the formation of this deposit would suggest the probability of its being gallic acid, but bloom is far less soluble in water than that acid. According to the author of the article on Tanning in the last edition of the *Encyclopædia Britannica*, this deposit consists of a portion of the gelatin from the interior of the skin, dissolved by the exhausted ooze which remains upon the surface by capillary attraction; and to avoid the waste and deterioration occasioned by its formation, it is recommended to remove the exhausted ooze by careful pressure. That such is not the constitution of bloom, however, seems to be pretty evident, from several circumstances. In the first place, it does not appear that the compound of tannin with gelatin or gelatinous tissue is capable of being dissolved to an appreciable extent by any quantity of the exhausted ooze, or of a strong solution of tannin (see note, page 223), such as that with which the hides which have been fully tanned in the handlers lie in contact, when in the bloomers or layers; and certainly tanno-gelatin could not be dissolved in this way, and reprecipitated in sufficient quantity to form such an abundant deposit as the bloomers and layers are found to contain when emptied. A specimen of this substance afforded me no traces of ammonia on destructive distillation, alone; when heated with fused potash, a faint trace of ammonia was disengaged, perceptible only by test-paper. Hence nitrogen, which enters into the composition of gelatin,

does not appear to be an essential constituent of bloom, and the nitrogen in the trace of ammonia disengaged in the above experiment was derived in all probability from some impurity. Moreover, a deposition of bloom, or, at all events, of a substance which is considered to be bloom by tanners, takes place from a tan-liquor which has not been in contact with gelatinous tissue.

A specimen of this substance examined by myself, a little darker in colour than ordinary bloom, was insoluble in hot and cold water, and in dilute muriatic acid; the greater part was readily soluble in a weak solution of potash, from which it was reprecipitated by muriatic acid. In concentrated sulphuric acid it dissolved, but was reprecipitated on the addition of water. The alkaline reaction of a solution of caustic potash on red litmus paper was completely prevented by applying an excess of this deposit; hence it may be considered to possess the characters of an acid. But it had not sufficient energy to displace carbonic acid from an alkaline carbonate. It was infusible, and burned with very little or no flame.

In each of these characters, this bloom possessed the closest resemblance to *ellagic acid*,* which is the yellowish-grey insoluble powder deposited, together with gallic acid, from an infusion of gall-nuts on

* Name derived from the French *galle* transposed. There is very little reason to doubt that the bloom found on leather which has been tanned by means of those materials only which contain the same variety of tannin as exists in gall-nuts, consists almost entirely of ellagic acid: but the nature of the bloom varies a little according to the variety of tannin made use of. When catechu is employed as the tanning agent, the bloom consists, according to Mr. Cooper, of catechuic acid, which forms the greater part of the portion of catechu insoluble in cold water.

exposure to the air. By boiling this precipitate in water, the whole of the gallic acid may be dissolved out. Ellagic acid is a product of the decomposition of tannin, and not of gallic acid, and it is not produced in any appreciable quantity from a *weak* infusion of gall-nuts. Admitting the identity of bloom and ellagic acid, or even a close analogy between these bodies, we hence perceive why the weaker "handlers," and nearly spent liquors, which are poor in tannin, but rich in gallic acid, afford no bloom; while the fresher and stronger "bloomers" and "layers," which are comparatively rich in tannin, yield an abundance of this deposit.

The prejudice of purchasers requires that both upper and sole leather should possess an uniform fawn colour; and, generally speaking, the quality of the leather is considered to be related in some degree to the colour, the best being lightest. This objection to dark-coloured leather consists, in reality, in an objection to leather prepared by the modern quick processes of tanning, and by either of the tanning agents which have been so extensively employed of late years in the place of oak-bark. The strong tan-liquors used in the quick processes always afford to the leather more colouring matter in proportion to tannin than the weak infusions used in the old process; and all the new tanning materials afford far more colouring matter than oak-bark. It is by no means certain, however, that dark-coloured leather is always of inferior quality.

The fresh infusions of all tanning materials contain more or less of a brown colouring matter, which

is capable of becoming permanently attached to the animal tissue; but the proportion of this colouring matter is greatly increased by the exposure of the infusion to certain chemical agents, the most important of which, so far as relates to the process of tanning, are alkaline bodies, and a source of free oxygen. Every tanner is acquainted with the fact that bodies of an alkaline nature, particularly lime, possess the property of instantly deepening the colour of his liquor to a very considerable extent;* and that though the very deep colour which pelt that contains unneutralized lime acquires at the commencement of the actual tanning disappears as the process advances, yet the colour of the leather thus prepared is always darker than that made from pelt which had been freed from lime as far as possible before being introduced into the tan-liquor. A solution of a caustic alkali, or an alkaline carbonate, added to a liquor not sufficiently concentrated to allow of the formation of a precipitate of tannate of the alkali, also produces a very considerable and an immediate deepening of the colour of the liquor.

Tanning infusions likewise become considerably darker in colour by exposure to the air through the absorption of oxygen, though the formation of colouring matter from this cause is slow; and hence frequently unheeded by the tanner. The constituents of the tan-liquors which are thus concerned in the production of colour are, for the most part,

* In the case of lime, the liquid actually becomes a little lighter in colour; the appearance of a deepening in colour being produced by the formation of a bulky precipitate, almost black, which remains for some time suspended in the liquor.

members of that class of bodies which have been designated "extractive matters," of the chemical history of which very little is known. The only distinguishing character assigned to extractive matters is the property of forming colourless or yellowish solutions in water, which, on exposure to the air, absorb oxygen and disengage carbonic acid, and thereby become converted into sparingly soluble substances of a dark brown colour, which were named *apothème* by Berzelius. But this property is possessed by several substances, which differ from each other considerably in other respects. All the varieties of pure tannin are susceptible of this change, to a greater or less extent; particularly the tannin of catechu, which is colourless or light yellow when pure, but rapidly becomes blood-red when freely exposed, in aqueous solution, to the atmosphere. Hence the circumstances which favour the formation of colouring matter should be avoided, for the sake of preserving the tannin as well as to prevent the leather acquiring a dark colour. It has been observed that an infusion of divi, prepared with little exposure to the air, is not nearly so dark-coloured as that made with free exposure; and that the colour of leather prepared by means of infusion of divi alone, in a closed vessel, as in the process alluded to at page 226, is unobjectionable, while the leather prepared by divi alone in the usual process is so dark as to be almost unsaleable. Every tanner is also acquainted with the fact that the uppermost hide in the tan-pits is always the most deeply-coloured; for which reason the same hide is not allowed to be the uppermost in two successive immersions.

The introduction of deoxidizing agents into the tan-liquors would no doubt retard, in some degree, the formation of colouring matters by the absorption of oxygen; but there is probably no substance of this nature which would not act injuriously on the tannin in some way or other, as, for instance, by precipitating it, or by exciting its fermentative decomposition.* The exclusion of the atmosphere, as far as possible, from the preparation of the infusion to the completion of the blooming, would doubtless be the most practicable and efficient method of preventing the production of so much colour.

I have been informed that the tanners of Scotland generally endeavour to limit the access of air to the tan-liquors as much as possible, but such is not the general practice of the English tanners.

One of the earliest invented of the processes for expediting the impregnation of hides, &c. with the tanning liquor, by the application of a mechanical force, was made the subject of a patent by Mr. Francis Spilsbury, in 1823.

The process of Mr. Spilsbury was conducted in the following manner. After being freed from hair and otherwise prepared by the ordinary methods, the hides were minutely examined to discover any accidental holes, which were carefully sewn up so as to render the hide water-tight. One of the hides to be tanned was stretched tight over the edges of a

* The employment of "vegetable matters and chemical agents capable of retarding oxidation, such matters or agents to be used with the tanning agent employed," is one of the claims in Mr. Warington's patent (page 205).

rectangular wooden frame; and on the hide was placed a second similar frame, which was screwed to the first frame by bolts passing through projecting ears. On the second frame was placed another hide; and on that, a third frame, which was tightly fastened to the others, so as to make the edges water-tight. The whole thus formed a flat water-tight vessel, bounded by the two hides and the middle frame. The apparatus was then placed in a vertical position, and tan-liquor admitted into the cavity between the two hides by a pipe leading from an elevated cistern, through an opening in the middle frame. The air in the vessel was allowed to escape by another opening in the frame, furnished with a stopcock, which was closed as soon as the bag became filled with tan-liquor. The pipe communicating with the bag and the cistern containing the tan-liquor was left open, to allow the hydrostatic pressure of the liquid column to force the solution through the pores of the hides by a slow infiltration, the liquid thereby making its appearance on the outsides of the hides like drops of dew. When the tanning was judged to be completed, the stopcock of the pipe from the cistern was closed, and the liquor drawn off by another stopcock; the bolts were then unscrewed, the frames removed, the compressed edges of the hides clipped off, and the hides finished off in the ordinary manner.

Some modifications of this ingenious process have been introduced, most of which, like the original, have been abandoned; the quality of the leather thus made being inferior to that made by the old method.

In the process patented by Mr. William Drake of

Bedminster, in 1831, the hides, prepared in the ordinary manner, were first slightly tanned in a weak liquor as usual, and two of about the same size and shape were carefully sewn together at their edges, so as to form a water-tight bag, in which the tan-liquor might be introduced, a small hole being left at one end for admitting the nose of a funnel. The bag thus made was placed between two vertical wooden racks, to prevent it from bulging at its sides when filled with cold tan-liquor, which was introduced through the aperture at the end of the bag, now the top. The bag being constantly kept distended, the liquid slowly penetrated to the outside of the hides in drops, which were collected and returned to the bag through the funnel. Towards the close of the process, when the hides began to feel hard, the temperature of the apartment in which the tanning was conducted was considerably raised, so as to facilitate the percolation of the liquid by promoting the evaporation from the exterior surfaces of the hides.*

In another process quite similar to the above, patented by Mr. Chaplin, the bags containing the tanning liquor were placed in an inclined position, and turned over at regular intervals, to equalize the tanning of the hides.

Neither of these infiltration processes has proved very successful; partly on account of the unequal permeability of hides, which allows of the percolation of the liquid and absorption of the tannin

* To prevent the formation of permanent indentations in the leather from the bars of the racks, it was necessary to shift the bags sideways a little occasionally. This inconvenience is avoided in the plan contrived by Mr. Cox, in which the bags are supported in a casing of canvass instead of wooden racks.

much more readily in some parts than in others. It has also been suggested that the excess of tannin to which the hides are exposed in these processes acts injuriously by dissolving a portion of the gelatinous tissue, which is found in combination with an excess of tannin as a slimy mass on the outer sides of the hides, the leather being thereby rendered lighter and more porous.* I am informed that the process of Mr. Chaplin, however, is still followed on an extensive scale (chiefly by himself), but the quality of the leather thus made is very inferior.

The first of the objections noticed in last paragraph does not apply to so great an extent to another mode of accelerating the impregnation of hides with tannin, which consists in suspending them in an air-tight vessel, from which the air is afterwards withdrawn by an exhausting pump, and the tan-liquor then admitted and forced into the pores of the hides by hydrostatic pressure. After a time, the tan-liquor, which should be weak at first, is withdrawn, the vessel again exhausted of air, and a fresh quantity of tan-liquor stronger than before, introduced. These operations may be repeated several times, with infusions increasing in strength, until the hides are completely tanned. Different

* This explanation of the formation of the slimy mass is offered by the author of the article on Tanning in the seventh edition of the *Encyclopædia Britannica*. I have not succeeded, however, in obtaining a solution of tanno-gelatin (made with infusion of nut-galls) in an excess of solution of tannin, although the aggregation of the precipitate into that peculiar tough, adhesive mass which it forms when stirred about in the liquid, was avoided. Tanno-gelatin may be easily dissolved, however, in a solution of gelatin.

processes of this kind have been practised by various tanners, the earliest introduced of which was made the subject of a patent by Messrs. Knowlys and Duesbury, in 1826. In all these vacuum schemes, the abundant evolution of bubbles of air or some other gas from the tan-liquors when admitted into the exhausted vessel, is found to be an inconvenience of no slight importance.

Another mode of tanning may be here alluded to, which consists of a combination of the old Danish plan with the modern infiltration process. In this, the hides or skins are sewn up into bags, filled with tan-liquor, and subjected to the hydrostatic pressure of a column of liquor, as in the processes of Spilsbury and Drake; but the bags are kept immersed in the tan-pit during the whole process, as in the Danish method.

An ingenious mode of causing the absorption of tannin to take place with more rapidity than in the ordinary process was made the subject of a patent by Messrs. Herepath and Cox, of Bristol, in 1837. The principle on which this method is founded, is that of washing a piece of cloth or a sponge, by allowing it to imbibe water, and then expressing the dirty liquid before the cloth or sponge is placed in clean water. As a sponge may be more readily cleaned by expressing the dirty water in its pores, and then allowing cleaner water to be absorbed, than by simply placing the sponge saturated with dirty water in clean water without expression, so the tan-liquors may be made to penetrate the hide more readily by squeezing out the impoverished liquor absorbed at one pit, before the hide is exposed to

the next pit in succession, than by transferring the hide at once from one pit to the next, with its pores saturated with a liquid which has been completely deprived of its tannin. The mode of compressing the leather to get rid of the impoverished infusion, adopted by the patentees, consists in passing the hides between two rollers, worked by steam or other power; the upper roller being pressed against the lower one with any required force by means of weighted levers. The lower roller, which is about thirty inches in diameter, is covered with horse-hair cloth; the upper one is only about eighteen inches in diameter, and is covered with woollen cloth. Between these rollers, a pair of which is erected over each tan-pit, the hides are drawn once a day, or oftener (not merely when they are transferred from one liquor to another); they being connected together, for this purpose, by strings so as to form one continuous belt. To form a tolerably uniform band, the hides are arranged alternately head to head, and tail to tail, or else, with the heads and tails towards one side alternately.

The time required for tanning a strong hide by this process is said to be from one to two months, and for kips and skins from three to four weeks. The thickest sole-leather, known as "butts," may be sent to the market within four months from the time of the receipt of the hides.

If the pressure to which the hides are exposed is not too great, the quality of the leather made in this way is good; but an excessive pressure produces a permanent condensation of the leather, which is fre-

quently found to be very injurious to the sale of the article thus made.

Of all the methods which have been suggested for the purpose of accelerating the process of tanning by mechanical means, that which seems to be entitled to preference is the following, as practised at the extensive tannery of Mr. Squire of Warrington. It is better adapted to the tanning of skins and kips for upper-leather, and various kinds of offal, than for that of hides for sole-leather. The prepared hides and skins are introduced with some of the fresh tanning material and a hot tan-liquor into a horizontal wooden cylinder, the length of which is about ten feet, and the diameter about five feet. The hides, &c., are introduced through an opening in the side of the cylinder, to which a water-tight lid is adapted, the vessel being about four-fifths filled; when the lid has been properly secured, the cylinder is rotated on its axis, at a velocity of about six or eight revolutions per minute, and is kept in a state of constant motion. The side of the cylinder is furnished, on the interior, with several short projecting ridges, for the purpose of increasing the agitation of the hides and preventing their becoming rolled into a ball. When the liquid and tanning material become exhausted of their tannin, which happens in a very short time, they should be removed and replaced by fresh materials and a hot liquor, since contact with a spent liquor is very injurious to leather.

The superiority of this process seems to arise from its presenting a combination of three conditions, of great importance in the operation of tanning, and

which are found united in no other process. These are, 1°, the constant agitation of the hides and skins; 2°, a warm tan-liquor; and 3°, the absence of atmospheric air. Through the motion of the skins and the heat of the tan-liquor, the time required for the combination of the animal fibre with tannin is considerably reduced, fourteen days being sufficient to tan thick kips perfectly; and as the access of air to the tan-liquor is almost completely prevented, the inconveniences which result from exposure to the air, particularly the formation of dark colouring matters, are in a great measure avoided. The colour of leather prepared with divi alone by this process is unobjectionable; but the infusion of the same material applied to the hides in uncovered tan-pits produces leather of a dark reddish-brown colour, sometimes quite unsaleable at the current prices. Leather prepared by the above process, however, is rather deficient in bloom.

In the best leather, the relative position and arrangement of the fibres is as nearly as possible the same as in the original hide or skin; and, in general, the greater the distortion of the fibres, the less durable is the leather. The section of a piece of weak leather prepared by some of the modern quick processes presents a much more perpendicular structure than that of leather made by the old method, and also than that of the original hide. This arises, in a great measure, from the hide becoming swollen in one direction only in the early part of the process, and not returning to its original thickness as the tanning advances.

The skin of the hog is difficult to tan completely, owing to the presence of a considerable quantity of fatty matter, not easily removed or saponified by lime. Saddles are usually made of the leather prepared from such skin. The human skin also requires a considerable time to be properly tanned. Horse-hides require a long treatment in the handlers, else the leather they afford is very liable to crack.

Of late years, a great quantity of thin and cheap leather has been made from hides split by a machine into halves; the half with the grain side, which produces the best leather, being used for shoes, and the half with the flesh side for inferior purposes. Great quantities of sheep-skins are also slit into halves; the grain side being used for preparing glove-leather, and the flesh side for wash-leather.*

The average cost of tanning thick sole-leather has been estimated at very nearly fourpence half-penny per pound of leather. Of this sum, threepence is con-

* Several years ago, a patent was obtained by Messrs. Bevington for a machine for splitting skins with the greatest certainty desirable, by which all the irregularities arising from the unequal thickness of the skin are confined to one of the halves, either the flesh or grain side, as may be desired. The skin to be split is extended quite flat and passed between two horizontal rollers, nearly in contact, and revolving slowly in opposite directions. Immediately opposed to the aperture through which the skin passes is the sharp edge of a long knife, which has a vibratory horizontal motion; by this the skin becomes divided into two thicknesses, one of which passes over, and the other under the blade. The thickness of the slices may be equal or unequal, according to the adjustment of the knife opposite the aperture between the rollers. In order to obtain one of the slices of uniform thickness and all the irregularities in the other, one of the rollers is made of several discs, so adjusted that any of them may move up or down a little, and thus allow an enlargement or a contraction of the opening between the rollers whenever the varying thickness of the skin which passes, renders it necessary.

sidered to be expended in the tanning material, and the remainder in labour, rent, lime, &c.

Since the selling price of sole-leather in butts is from ninepence to eighteen-pence per pound, and the average cost of tanning fourpence halfpenny per pound, it is obviously to the pecuniary advantage of the tanners to cause the hides to combine with as much tannin as possible, without injuring the quality of the leather. All leather prepared in the ordinary manner contains a considerable quantity of tannin more than is necessary for the complete saturation of the gelatinous tissue. This excess is not chemically combined with the tissue, but merely mechanically attached to the exterior of the fibres, in the same manner as soluble colouring matters become attached to animal charcoal. By digesting clippings of leather in water, some of this mechanically attached tannin may be dissolved out.

A patent has been recently obtained by Mr. Julius Bordier for a process for converting hides and skins into leather, by impregnating them with some metallic or earthy substance, in the place of tannin. This process is an application of one like that of *tawing*, which has hitherto been practised only on light skins for the preparation of glove and fancy leathers, to heavy skins. Instead of alumina, however, which is the earthy substance imparted to the

Since only one of the rollers is capable of yielding in this way, it follows that all the irregularities will be found on the side of the skin in contact with that roller, the thickness of the other side being uniform. The time required for splitting a sheep-skin of average size by one of these machines at Messrs. Bevington's is two minutes.

skin in the process of tawing, the patentee prefers a preparation of a body of the same nature, namely, peroxide of iron. By this process the preparation of thick sole-leather may be completed in a fortnight or three weeks. The leather thus made is said to be more durable than that produced by the ordinary means.

After having undergone the ordinary operations of washing, unhairing, and swelling, the hides and skins are ready to be submitted to the action of the earthy or metallic solution. The preparation which is considered to be best adapted for the impregnation of hides is the subsulphate of the peroxide of iron, that is, a compound of sulphuric acid and peroxide of iron, containing an excess of the latter constituent. To prepare this substance, two hundred-weight of bruised copperas may be dissolved in about fifteen gallons of boiling water contained in a copper boiler. When the solution is complete, it is run off into a wooden vat, not very deep, of the capacity of about forty-four gallons, where it is mixed, first, with about forty-four pounds of sulphuric acid of spec. grav. 1.848, and after agitation, with forty-four pounds of finely powdered black oxide of manganese, added by degrees. The agitation should be continued until the disengagement of gas ceases, and be afterwards repeated at intervals, until the mixture is cold. The solution may then be diluted to any required strength by the addition of water. Instead of using concentrated sulphuric acid, two hundred-weight of pounded copperas may be dissolved in a leaden boiler, in sixty-six pounds (avoirdupois) of unconcentrated sulphuric acid (of

spec. grav. 1.530), and one hundred and thirty-two pounds of water. Another process for preparing a solution of the subsulphate of peroxide of iron is described by the patentee, in which the peroxidation of the iron is effected by means of nitric acid instead of peroxide of manganese. Before being applied to the hides or skins, these solutions are always considerably diluted with water. When digested in the liquor thus made, the hides and skins gradually become impregnated throughout their entire thickness with an insoluble subsulphate of the peroxide of iron, while free sulphuric acid, sulphate of manganese, and a little protosulphate of iron (copperas) remain in the liquid, unabsorbed. From six to eight days are said to be a sufficient time for the complete impregnation of hides, and three or four days for the impregnation of skins. The effect of the subsulphate of iron on the animal fibre is to render it completely imputrescible; but the leather, when taken out of the liquid, is as permeable to water as that tanned by the ordinary processes. The requisite impermeability, and the proper degree of toughness and tenacity, are afterwards imparted by the process of currying.

Similar in principle to the above method of preparing leather is a proposed mode of preserving hides and skins which are intended to be afterwards tanned in the ordinary manner, instead of drying or salting. This method consists in subjecting the fresh hide or skin to the action of corrosive sublimate, which, when applied in solution, would combine with the animal fibre, and render it imputrescible. The practical superiority of this to the common modes of preserving

hides seems to be of a particularly doubtful character: for not only would a considerable quantity of corrosive sublimate be required to effect a complete preservation (compared with the quantity of the same substance required for preserving wood, as in Kyan's process), but the mercurial compound which combines with the hide would afterwards be found difficult of displacement by tannin.

Currying.—Sole-leather is fitted for the purposes of the shoe-maker in the state in which it is sent out by the tanner, but leather intended for the upper parts of boots and shoes, for coach-makers and for saddlers, has to undergo certain operations by the currier, for the purpose of giving it the necessary impermeability to water, smoothness, softness, colour, lustre, &c. The currier first moistens the leather with water, then* places it on an inclined plane called the "horse" (similar to the beam, fig. 29, page 196, but flat instead of curved), and shaves off all the superfluous thicknesses by means of straight, two-handled knives, called "cleaners." Two or three of these are used, of different degrees of sharpness. The leather is then wetted and rubbed on the grain side with pumice or grit-stone, whereby the superficial coating of bloom becomes removed. The next in succession of the currier's operations has the effect of rendering the leather extremely flexible. This consists in rubbing it on each side successively with an instrument called the "pommel," which

* Formerly, after moistening the leather, and before equalizing its thickness by shaving with the "cleaners," it was common to beat it upon a strong hurdle with a heavy mallet, called the "mace." This is not, however, the present practice.

consists of a piece of hard wood, flat on the upper side and rounded on the lower, capable of being fixed to the hand by a leather strap. The lower surface of this instrument is covered with a number of transverse parallel grooves. After being thus rubbed, the leather is once more scraped with a broad knife, to equalize its thickness, and is then "dubbed" with oil, tallow, a composition of lamp-black and unctuous matters, or some other greasy material, according to the quality of the leather, and the purposes for which it is required. It is, lastly, polished by means of hard wooden rubbers.

Such is a general view of the principal operations of which the process of currying consists; but they are considerably varied in their details, according to the kind of leather operated on, and the uses to which it is to be applied. Shoe leather is blackened on the flesh side, but for some purposes leather is blackened on the outer or grain side; in which case it is moistened with a solution of copperas in water, which gives rise to the formation, on exposure to the air, of the black tannate of the peroxide of iron.

§ IV. PREPARATION OF LIGHT AND FANCY LEATHERS.

The different varieties of fancy or light leather may be arranged into three classes, distinguished from each other by peculiarities in the mode of manufacture. These are, leather tanned by means of sumach, tawed leather, and oiled leather. The most important of the varieties of leather tanned by means of sumach only is *Morocco leather*, of which a great

quantity is used for chair-covers, coach-linings, book-binding, case-making, ladies' shoes, &c. *Roan* and *skiver* are two other varieties of sumach leather; the first of which is used for book-binding, and for making shoes and slippers, and the other for pocket-books, hat-linings, work-boxes, &c. Tawed leather is chiefly used for making ladies' shoes and common gloves; and oiled leather for making riding gloves, and as wash-leather.

Morocco leather. *—The finer kinds of Morocco leather ("true Morocco") are always prepared from goat-skins; but the inferior, or "imitation Morocco," is made from sheep-skins. The routine of operations to which goat-skins are subjected preparatory to the actual tanning differs little from the common processes of cleansing and unhairing hides and skins, as described in a previous section. After being soaked in water for several days, and scraped on the flesh side, they are generally soaked in lime-water for about a month; during which time they are frequently taken out of the liquid, allowed to drain in a heap, and again immersed, in order to equalize the action of the lime. When the hair can be easily pulled off with the fingers, the skins are unhaired upon the beam in the usual manner (page 194); after which they are again soaked in lime-water for a day or two, and then fleshed. Before being exposed to the tanning infusion, the skins are freed from the

* An interesting and sufficiently detailed account of the modes of preparing Morocco and other kinds of fancy leather followed at the Neckinger Mills, Bermondsey, is contained in "A Day at a Leather Factory," forming No. 8 of the first series of "Days at the Factories," and No. 652 of the Penny Magazine.

greater part of the lime contained in their pores by being digested in a lixivium of hen-dung or some such impure alkaline solution; after which they are well scraped and again immersed in the liquid. Each skin is then sewn up into the form of a bag, with the grain side outwards, only a small hole being left, sufficient for the introduction of the nose of a funnel; and each bag is nearly filled with a strong decoction of sumach. The bag having been completely distended by blowing into it, in order to free it from wrinkles and enable it to float on water, is thrown with several others into a large shallow vessel filled with a weak infusion of sumach, in which it is kept for about three or four hours, being occasionally moved about by manual labour. Once during this process the bags are taken out, compressed by being piled in a heap, and again subjected to the tanning liquor. When the tanning is completed, the skins are unstitched, rinsed, rubbed out as smooth as possible on a sloping board, and lastly, hung up to dry. When quite dry, they are ready for the process of dyeing,* the principles of which are precisely the same as those of cotton, silk, and wool-dyeing operations. The mordant, which is usually a preparation of either tin or alum, is first applied (if any is required); and afterwards the colouring infusion, as decoction of cochineal to produce a crimson and scarlet, or decoction of logwood to produce a puce colour. A blue colour is imparted by a solution of sulphate of indigo or by the common blue-vat; violet, by cochineal-red and a

* At some leather-factories the dyeing is sometimes performed before the tanning.

light indigo-blue applied consecutively; and black, by a solution of dyer's iron-liquor (acetate of iron) applied to the grain side only. As this leather is in general required to be dyed only on one side, it is usual to place two skins in close contact before dyeing, the sides coloured being outermost. After being thus dyed, rinsed, sometimes slightly oiled on the grain side, and thinned upon the flesh side, the skins are subjected to a kind of currying process, by which their original softness and pliability are restored. This consists either in passing them in a humid state two or three times in different directions between two cylinders revolving nearly in contact; or in rubbing them by the hand with instruments of different degrees of hardness, one of which is a small wooden ball or roller having on its surface a number of fine parallel grooves, which impart to the Morocco the peculiar grain which distinguishes that kind of leather. A surface of cork is sometimes used as the last rubber for Morocco leather.

The routine of operations followed in the preparation of "imitation Morocco" from sheep-skin is much the same as that described above. But whether these kinds of skins are tanned by means of sumach for making Morocco, or by means of oak-bark for making common leather, they are almost always passed through a powerful press (after having been stripped of their wool by the fellmonger) that the greater part of the unctuous matters with which they abound may be expelled. If allowed to remain, these matters would materially impede the action of the tan-liquor.

Skiver and Roan.—The kind of leather called skiver is prepared from sheep-skins split by machine when in the state of pelt, and tanned by means of sumach. Being more easily penetrated by the tanning infusion than whole goat-skins, these split skins are not commonly sewn up into bags like the former, but are immersed in the liquor in the open state. Roan is generally prepared from sheep-skins by means of sumach, in just the same manner as Morocco; but this kind of leather does not present the grained appearance of Morocco leather, imparted by the grooved ball or roller.

The “enamelled leather” used for ladies’ shoes, belts, &c., is also prepared by means of sumach, the skin being either that of the calf or the seal. The gloss is communicated by a peculiar varnish.

Leather prepared by means of alum (kid-leather).—The process of preparing alumed leather is technically known by the name of “tawing.” The skins which are made the subjects of this process are those of the kid, the sheep, and the lamb; and the resulting leather, which is particularly soft, is mostly used for gloves, and shoe-linings. The principal operations in this art, as practised on kid-skins, are, 1°, soaking the skins in water for a few days, for the purpose of softening them; 2°, “breaking,” or scraping with a blunt knife on the flesh side, the skins being laid upon the beam; 3°, liming for about a fortnight, and unhairing and fleshing in the usual manner; 4°, soaking in a fermenting mixture of bran and water, and “striking” on the beam with an iron instrument, for the purpose, principally, of

removing the lime;* 5°, soaking for a few minutes either in a mixture of alum and common salt, dissolved in water, or in a mixture of solution of alum and salt, with flour and yolk of eggs; and 6°, washing, drying, and "staking."†

The aluminous compound, by combining with which the skins become converted into leather, is considered by Berzelius to be a subchloride of aluminum. By the re-action of common salt (chloride of sodium) and alum (sulphate of alumina and sulphate of potash), there are produced chloride of aluminum, sulphate of soda, and sulphate of potash: the chloride of aluminum becomes resolved by the skins into a subchloride and a perchloride; the former, which is the least soluble, combines with the animal tissue; while the latter, together with the sulphates of soda and potash, remains in solution in the liquid.

Flour and yolk of eggs are added to the mixture of alum and salt only in the preparation of the finer kid-leather, the beautiful softness of which is attributed to the use of these materials. One hundred skins require from six to eight pounds of alum, and about as much salt; and for fine kid-leather, the yolk of one egg may be employed for each skin. The impregnation of the skins with the emulsion is commonly effected in an open tub, the mass being either worked about by the hands, or

* This is probably effected by the solvent power of the acetic acid contained in the bran-water.

† The operation of staking consists in forcibly drawing the skin by the hand over the edge of a semi-circular iron plate, fixed upright, with its round edge uppermost, to the top of a wooden stake about two feet six inches in height. By this scraping the skins become rendered soft, and smooth.

trampled upon with the naked feet. Sometimes the mixture and skins are introduced into a small barrel (as in the tanning process described at page 226) through an opening in the curved side, and the mass is agitated by rapidly rotating the barrel.

The preliminary operations to which lamb-skins are subjected in the preparation of imitation kid-leather differ from those above described. After having been steeped in water and scraped on the flesh side, the skins, which are supplied to the leather-dresser with their wool still on them, are allowed to undergo an incipient putrefaction, to loosen the roots of the wool, by being suspended for from four days to a week in a close room, protected as much as possible from the vicissitudes of the atmospheric temperature. The softening of the roots of the wool cannot be conveniently effected by the application of lime, as that material would exert an injurious action on the wool itself, which is disposed of to hatters for making the bodies of common hats. After the skins have been scraped on the flesh side and deprived of their wool, they are steeped in lime-water, fleshed, soaked in fermenting bran-water, and then exposed to the mixture of alum and salt, as already described.

When tawed with the wool on, as for mats and similar articles, the sheep-skins are doubled, with their wool side inwards, so as to expose only the flesh side to the tawing mixture. Calf and other skins with their hair still attached are also occasionally converted into leather.

Chamois leather.—The peculiarity in the prepa-

ration of chamois leather, or the process of "shamoying," consists in the application of oil to the skin in the place of tannin or a preparation of alum. Formerly, leather was prepared in this way only from the skin of the chamois-goat, but the skins of sheep, deer, and other animals are now subjected to the same process. The mode of preparation is just the same, whether for fine chamois leather or for that coarser kind known as wash-leather. After having been subjected to the usual preparatory operations of washing, liming, scraping, and fleshing on the beam, and steeping in fermenting bran-water to remove the lime, the skins are wrung and then beaten as dry as possible, in the trough of a fulling-mill, similar to that used in the woollen manufacture, the two hammers of which fall on the skins in succession. Having been thus beaten until quite dry to the touch, the skins are ready to be impregnated with oil; for which purpose cod-oil is generally used, but any cheap animal oil may be employed. In some leather-factories the skins are taken out of the mill, exposed for a short time to the air, besmeared separately with oil, and then returned to the mill, that the oil may be beaten into the pores of the skins; the airing, oiling, and fulling being several times repeated. But in other factories, at the Neckinger mills, for instance, the oil is poured in small quantities at a time upon the skins while in the mill. When the oil first applied has been entirely absorbed, the skins are taken out of the mill, extended flat, and exposed to the air for a short time; after which they are returned to the mill, and beaten with a fresh quantity of oil. This is repeated several

times, until from two to three gallons of oil have been absorbed by one hundred skins. When thus fully impregnated with oil, the skins are allowed to undergo a slight fermentation, which is considered to cause a more intimate combination of the oil with the animal fibre, and which also probably acts beneficially by destroying some easily decomposed constituent of the skin, the putrefaction of which at another time would be less manageable. This fermentation sometimes requires to be assisted by the application of a slight heat. The skins are lastly immersed in a weak solution of potash, which serves to remove the redundant oil, by forming with it a soluble saponaceous compound.

A considerable quantity of chamois leather is prepared from the least regular portion of split skins; the other part, which is of uniform thickness, being either tanned by sumach or tawed by alum and salt. The grain side of the skins is usually removed previous to the application of the oil, by scraping with a knife or rubbing with pumice-stone, whereby a softer surface is obtained. In the process of making oiled leather, the animal tissue undergoes much less alteration than in the tanning and tawing processes. The oil, in fact, produces no chemical alteration of the fibre; and the indisposition of the latter to putrefy may be referred in a great measure to the thorough expulsion of the fluids and the constituents of the skin, soluble in cold water, through the action of the fulling stocks. That the gelatinous tissue undergoes no essential alteration is evident from the circumstance that chamois leather may be easily resolved into glue by the action of boiling

water. Of late, a kind of leather has been prepared by first slightly tanning the skins in the ordinary manner by means of an infusion of willow bark, and afterwards impregnating them with oil in the fulling mill.*

Russia leather.—In Russia, this variety of fancy leather, which is valued on account of its not being subject to mould when kept in a damp situation, and also from being repulsive to insects, is prepared by tanning the skins of calves, sheep, and goats with a warm decoction of willow-bark, then dyeing them of a reddish colour by a decoction of red sanders wood, and afterwards applying, by a sort of currying process, an empyreumatic oil prepared by distilling the bark of the birch-tree, which imparts the peculiar odour by which this kind of leather is distinguished. The loosening of the roots of the

* The importance of the English chamois leather manufacture has experienced a considerable decrease of late years. In reference to this subject, Mr. Aikin made the following statement, in one of his lectures before the Society of Arts. "Till a few years ago, there was an immense quantity of the skins of sheep, goats, and deer shamoyed in England. Breeches of this article, either white or dyed, were commonly worn by persons whose occupations or amusements led them to be much on horseback. They were worn by most of the cavalry of Europe; and the English shamoyed leather, being of extraordinary good quality, was employed in clothing, not only our troops, but the cavalry of Prussia, Austria, and most of the other German States. In the campaigns in Spain, during the last war, it was discovered by the British commander that the health of the horse-soldiers was seriously affected, in wet weather, by the leather that they wore; which, fitting close to the skin and being long in drying, chilled the men, and rendered them liable to rheumatism and other diseases. Woollen cloth was accordingly substituted; and as an example having been followed by Austria and Prussia, this change occasioned a great decline in that branch of the English leather

PREPARATION OF LIGHT AND FANCY LEATHERS. 243

hair or wool, preparatory to tanning, is said to be effected by soaking the skins in a weak wood-ash lye, the active constituent in which is carbonate of potash.*

* The use of a solution of carbonate of soda or carbonate of potash, for soaking hides and skins in order to facilitate the removal of the hair, was one of the subjects of a patent granted in this country a few years since.

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CAOUTCHOUC;

ITS PROPERTIES AND APPLICATIONS.

THE extraordinary properties which caoutchouc possesses have acquired for this remarkable substance a great number of interesting applications in the arts and manufactures, in which no other known substance can be employed as an efficient substitute.

Caoutchouc is derived from the juices of several Asiatic and American trees, particularly *Ficus elastica*, *Jatropha elastica*, and *Urceola elastica*. It may also be obtained from the juices of the *Smilax caduca*, *Asclepias vincetoxicum*, *Ficus religiosa*, and several other trees. The Asiatic caoutchouc is derived, for the most part, from the *Ficus elastica*,* and the South American and West Indian from the *Jatropha elastica*.

In the cooler seasons of the year incisions are made around the tree, completely through the bark,

* The *Ficus elastica* is larger than any of the other trees in the extensive forests in which it abounds, and may be recognised at a distance of several miles by the picturesque appearance produced by its lofty and dense crown. It grows either solitary or in groups of two and three. The circumference of the trunk of one was found to measure no less than seventy-four feet, and the height of the central tree of a group of three was one hundred feet. It has been computed that there are more than forty-three thousand of these trees within a length of thirty miles and breadth of eight miles of forest near Ferozepoor in the district of Chárdwár, in Assam (Mr. William Griffiths).

and the milky juice which exudes is immediately applied in successive layers to moulds of unburnt clay, each layer being dried either by exposure to an open fire or to the air and sun, previous to the application of the next layer. When the coating is judged to be sufficiently thick and dry, the clay mould, which, in the West Indies and South America, has usually the form of a pear, is broken, and the fragments are withdrawn through the neck; the caoutchouc thus comes to have the form of a flask, in which state it is exported. From the East Indies caoutchouc is exported in the form of large junks and balls, lighter in colour than that brought from South America, which are obtained by allowing the juice to inspissate by exposure to the sun. The juice itself has of late been imported into Europe in small quantity, in closely stopped vessels. If kept cool and carefully protected from the air, it may be preserved for a considerable time without solidifying. The juice afforded by old trees is said to be much richer in caoutchouc than that got from young trees, and that drawn in cold seasons richer than that drawn in hot. The incisions are repeated once a fortnight, and are not confined to the trunks; but are extended to the larger branches, even to the top of the tree. According to Mr. Griffiths, the richest juice is extracted from the larger reflex roots, which are half exposed above ground.*

The juice is of a pale yellow colour, and has the consistence of cream. It is readily miscible with water and with alcohol, but not with the proper

* A specimen of the juice analyzed by Mr. Faraday, contained the following ingredients : Water,

solvents for caoutchouc, as coal naphtha, and the liquid which caoutchouc itself affords on destructive distillation. If exposed to the air, it acquires a sour odour from the putrefactive decomposition of the nitrogenized matter which it contains; and if in a thin layer, it affords in a few days a solid deposit of elastic caoutchouc. On the application of heat to the juice, the suspended caoutchouc aggregates, and may be obtained in a tolerably pure state by being merely washed in water and dried by pressure between folds of cloth. To obtain pure caoutchouc in this way, it is convenient to mix the juice with four or five times its volume of water before applying heat.

As imported, caoutchouc is always more or less impure, and is sometimes fraudulently mixed with earthy matter. The dark colour of South American and West Indian caoutchouc is derived, for the most part; from the smoke of the fire over which it was dried; when quite pure, it is transparent, colourless, and inodorous. When a bottle of caoutchouc is cut, the layers are distinctly visible; and if a mass is soaked in boiling water, they may even be detached.

Water, containing a little free acid	56·37
Caoutchouc	31·70
Albumen	1·90
Wax	a trace
A nitrogenized body soluble in water	7·13
A substance insoluble in water	2·90
	<hr/>
	100·00

Two samples of caoutchouc juice, examined by Dr. Ure, did not afford any appearance of coagulum when mixed with alcohol of sp. gr. 0·825. It is hence inferred that albumen is not an essential constituent of the juice.

When a piece of caoutchouc is suddenly stretched, it becomes warm, and also electrically excited. After having been digested in warm water, it may be extended to seven or eight times its original length without having its contractile power destroyed. If a bottle of caoutchouc is softened by a slight soaking in sulphuric ether, or by long boiling in water, it may be inflated by means of a syringe, or by the mouth, until it becomes so thin as to ascend if filled with hydrogen gas. If the bag is dried while in the expanded state, it does not contract on making a puncture for the air to escape. A bag has been made in this way of between six and seven feet in diameter.

If exposed to temperatures near the freezing point of water, caoutchouc becomes hard, possessed of little elasticity, and much more opaque than when warm. Long quiescence at common temperatures produces similar changes. If a thin sheet in this state is exposed to a gentle heat, it softens, and at the same time becomes more translucent, as if from the liquefaction of a constituent which is solid at low temperatures.*

* Some interesting observations were made by Mr. Gough of Kendal on the connection between the elasticity of caoutchouc and its temperature (Thomson's Organic Chemistry, Vegetables, p. 696). If a soft thong of this substance, of two or three inches in length, and a few lines in breadth and thickness, is forcibly stretched and applied to the lips, a very sensible increase of temperature may be perceived; but on allowing the thong to relax to its former state, there is a slight production of cold. If a thong is stretched, plunged immediately into cold water, and kept extended for a few minutes in the liquid, it loses much of its contractile power, not returning to its former dimensions when allowed to relax. But if now plunged into warm water, or if held for a short time in the warm hand, it absorbs heat, begins to contract, and is soon reduced to its former figure and size.

Before

When heated to about 248° , caoutchouc melts, and remains viscid for a considerable time. It is sometimes used as a lute in this state where a high temperature is not required, but a considerable time elapses before it regains its original solidity. It immediately inflames by contact with a lighted taper, and burns with a white flame and much smoke, emitting at the same time a peculiar and rather offensive odour. At Cayenne, in Guiana, and some other countries where caoutchouc is readily obtained, it is made into torches, which afford a very good light.

Caoutchouc is quite insoluble in water, both hot and cold. If boiled in water for a considerable time, it softens and swells up, and the dark-coloured caoutchouc becomes translucent on the edges from the removal of the foreign impurities. If two pieces are pressed together for some time in this soft state, they unite as firmly as if they formed one piece.*

Before threads of caoutchouc can be adapted to a textile manufacture, they must be deprived of their elasticity. This is effected by stretching the thread to seven or eight times its original length (whereby it becomes extremely hot), and keeping it extended (on a reel) for a fortnight or three weeks. It may then be worked, and the elasticity may be immediately restored at pleasure by the application of a gentle heat.

Caoutchouc suffers an increase in density by being extended. The specific gravity of a thread stretched to seven or eight times its original length, and kept in that state for a fortnight or three weeks to deprive it of contractile power, was found to be 0.948732. When the elasticity, and with it the original length, was restored by warming the thread in the hand, the specific gravity increased to 0.925939 (Dr. Ure).

* Caoutchouc tubes, which are of great service in the laboratory for connecting different parts of a pneumatic apparatus, may be easily made by fastening a piece of sheet caoutchouc tight around a glass tube and boiling it for some time in water. A more expeditious method of making the tube consists in folding a piece of sheet caoutchouc round a cylinder, and cutting off the superfluous edges with a sharp and clean

Caoutchouc may be digested in alcohol for a considerable time without being dissolved or altered, but at length it becomes soft, though no portion is dissolved. In ether, which has been well washed to remove any alcohol that may be present, caoutchouc dissolves with facility; and when the solution is evaporated at common temperatures, the caoutchouc is obtained unaltered, but with a fresh adherent surface like that presented by a recent cut. An ethereal solution of caoutchouc may therefore be employed for making instruments of this substance of any form, as the milky juice of the *Ficus elastica*, but the expense of ether in this country would be a material impediment to the extensive adoption of such a method. Other solvents will be noticed presently, equally efficient and far less expensive.

At common temperatures the concentrated mineral acids have little or no action on caoutchouc. Oil of vitriol, in the cold, only carbonizes it superficially; but on the application of heat the caoutchouc is completely decomposed, carbonic acid and sulphurous acid gases being evolved. Muriatic acid is without action on caoutchouc; nitric acid, with the aid of heat, decomposes it with evolution of nitrogen and carbonic acid gases, and oxalic acid remains behind. The caustic alkalies act slowly on caoutchouc, rendering it soft and glutinous, and dissolving it in small proportions with the assistance of heat.

Caoutchouc belongs to the class of hydrocarbons,

pair of scissors, and then carefully pressing together the clean fresh-cut edges. If quite free from dirt and not ragged, the fresh edges unite firmly, and produce a perfectly air- and water-tight joint.

but some uncertainty exists as to its exact composition, from the difficulty of obtaining it in a perfectly pure state. An analysis by Mr. Faraday afforded results which correspond to 8 eq. of carbon and 7 eq. of hydrogen; and another, by Dr. Ure, to 3 eq. of carbon and 2 eq. of hydrogen.

Caoutchouc is dissolved by linseed and other fixed oils, but such solutions do not afford a deposit of caoutchouc on exposure to the air.

It is also soluble in many essential oils, and the solutions leave, on evaporation at a gentle heat, a residue of caoutchouc, which, from the greater number of oils, remains glutinous for a considerable time, and is not therefore adapted for all the applications of this substance in its ordinary state. It happens, however, that from oil of turpentine the caoutchouc is obtained as firm and solid as it was before being dissolved. The turpentine solution, in fact, may be employed for any of the purposes to which the ethereal solution or the juice of the *Ficus elastica* is applicable. Aided by a moderate heat, the caoutchouc being cut into small shreds, and the mixture contained in a close vessel, the solution takes place with facility; a dark viscid liquid is obtained, which may be applied by a brush to any surface to which a coating of caoutchouc is to be imparted. If assisted by a gentle heat, the desiccation takes place rapidly, and the caoutchouc remains perfectly solid. Any inconveniences which arise from the adhesiveness of the fresh surface may be obviated by sprinkling on it a very small quantity of a fine powder, such as dry starch.

A liquid more commonly employed as the solvent

of caoutchouc is coal naphtha or coal oil, which is a product of the distillation of coal tar. The solvent power of this liquid on caoutchouc was first observed by Mr. Mackintosh, and applied by him on an extensive scale for the production of a textile fabric impervious to water. The chief inconvenience which attends the employment of this liquid is the disagreeable odour which it permanently communicates to the goods.

When caoutchouc is digested in its own weight of hot naphtha, it swells up to more than thirty times its original bulk ; and forms a thick glutinous mass, from which, when exposed in a thin layer to the air, the naphtha soon volatilizes, and leaves a solid and firm deposit of caoutchouc. To make the solution on the large scale, about half a ton of caoutchouc, cut into small lumps, is introduced into a cast-iron pot, of nearly four feet in diameter, furnished with a revolving shaft of wrought iron, about four inches in diameter, for the purpose of agitating and rubbing the caoutchouc. A quantity of coal naphtha, somewhat less in weight than the caoutchouc, is then introduced, and the box is closed with a lid. The solution is effected in two or three days. The application of external heat is unnecessary, as sufficient heat is generated by the attrition.

The common water-proof cloth, consisting of two pieces of cloth with an interposed layer of caoutchouc, is made in the following manner. One of the pieces of cloth is drawn horizontally between two wooden bars, the upper of which is faced with steel, and the caoutchouc solution is thickly plastered on the cloth by a wooden spatula, as it advances

towards the bars. The two bars are so adjusted as to leave a very narrow slit between the cloth and the upper bar, whereby the caoutchouc solution is distributed evenly over the surface. The cloth is next suspended in a well ventilated apartment for a few days to dry, after which a second and a third coating are applied in a similar manner.

Two pieces of cloth, thus prepared and nearly dry, are brought evenly into contact with their caoutchouc surfaces face to face, and immediately passed between two wooden rollers with pressure, whereby the caoutchouc surfaces become strongly adherent. The cloth is lastly suspended until quite dry, and freed as much as possible from the disagreeable odour of the naphtha.

A fabric of a similar nature to the preceding has been lately substituted for leather in the fillet cards for the cotton and tow manufacturers. It consists either of several alternate layers of strong cloth and caoutchouc, or of two sheets of caoutchouc with a piece of cloth interposed, or of two pieces of cloth with an interposed sheet of caoutchouc.

From the extreme adhesiveness of the fresh surface of caoutchouc, the naphtha and turpentine solutions may often be employed with advantage as a cement. Thus a very thin layer of caoutchouc carefully applied to the back of a book is sufficiently adherent to bind the leaves together firmly, without the trouble of stitching or sewing. In the patented method of binding books by means of caoutchouc (invented by Mr. William Hancock) the sheets are folded in double leaves, and when properly arranged in a press, the caoutchouc solution is applied

three or four times to the back, one coating being dried previous to the application of the next. The band of cloth for the back and sides is then cemented to the book with the caoutchouc solution; after which, the boarding is completed in the ordinary manner.

Caoutchouc is the basis of one of the preparations known as Jeffrey's Marine Glue, which is formed by adding to a solution of one pound of caoutchouc in four gallons of crude naphtha, made in the cold with occasional agitation, shell lac or gum lac in the proportion of two parts by weight of lac to one part of the solution, and the mixture is heated and stirred in an iron vessel provided with a tap at its lower part. When the caoutchouc solution and lac are thoroughly incorporated, the mixture is drawn off by the tap while hot, and poured out on slabs to cool. When required for use, it is heated to about 250° Fahr., and applied as ordinary glue. As this cement is not liable to be softened by water, like common glue, it is very valuable for uniting pieces of wood, &c., which are to be submerged in water.

When caoutchouc is heated in a distillatory apparatus to a temperature considerably above its melting point, it is decomposed, and the greater part is resolved into a vapour, which is capable of being condensed into a mixture of several oily liquids, some of which are possessed of very remarkable properties. The mixture is generally known by the name of *caoutchoucine*.

The proper temperature at which the distillation should be performed is about 600° Fahr. A dark-coloured oily liquid distils over, to the amount of about

eighty-three parts from one hundred of caoutchouc, nothing remaining in the still or retort but charcoal and the dirt of the caoutchouc. The process of distillation is facilitated by mixing the caoutchouc with some of the liquid distilled at a previous operation, in the proportion of one part of the liquid to two parts of caoutchouc.

When the dark-coloured product of the first distillation is subjected to several re-distillations, it becomes limpid and colourless. By changing the receiver as the distillation advances, and the temperature of the boiling point rises, the liquids which constitute the mixture may be separated to a great extent through their great difference in volatility: the most volatile constituent boils at about 90°, and the least volatile at about 680°.

The chemical composition of these oily liquids has been made the subject of investigation by Dr. Dalton, Dr. Gregory, Himly, and Bouchardat. According to Himly, they are all composed of carbon and hydrogen in the proportion of five eqs. of carbon to four eqs. of hydrogen, which is the same proportion as exists in oil of turpentine. By careful rectification he obtained one liquid, the boiling point of which was constant at 339° Fahr., to which he applied the name *caoutchine*. Its specific gravity was 0.842. Another portion, which boiled at 97°, was found by Dr. Gregory to have very nearly the same composition as olefant gas, that is, the same number of equivalents of carbon as of hydrogen. When this liquid was treated with sulphuric acid, it became black, evolved sulphurous acid, and on the addition of water yielded another oil of the

same composition, which boiled at a temperature above 428°.

By surrounding the receiver with a freezing mixture, Bouchardat obtained a liquid, the boiling point of which was below 32° Fahr., to which he applied the name *caoutchène*. This is supposed to be identical with one of the products of the destructive distillation of oil, recognised as a distinct substance by Mr. Faraday, having the same composition in one hundred parts as olefiant gas. Its specific gravity was so low as 0·654. After the more volatile oils distilled over, there remained behind in the retort a liquid, which has received the name of *hevéène*, the boiling point of which was 599° Fahr. Its sp. gr. was 0·921. It was found by Bouchardat to have the same composition as caoutchène.

The mixture of these liquids, or caoutchoucine, is an excellent solvent of caoutchouc, and also when mixed with some strong alcohol, of the various resins, especially of copal, which it dissolves without the aid of heat. It readily mixes with oils, causing them to become more fluid, and as it evaporates quickly is found to be a useful vehicle in some cases for oil-paints. Mr. Barnard procured a patent in 1833 for its applications in the arts; but the low price of coal naphtha, compared with that of caoutchoucine, must prevent the latter from being largely employed as a solvent of caoutchouc.

The caoutchouc stoppers for bottles, for the manufacture of which a patent was obtained by Mr. Brockedon, are made in the following manner. Wool, cotton, or other fibrous material, is felted into a roll

of the diameter and length required, and to such a degree of hardness as will leave the stoppers sufficiently soft and elastic. The roll is then coated with a solution of caoutchouc (either in naphtha or turpentine), which is allowed to become nearly dry; and over the fresh surface of caoutchouc thus obtained is laid a piece of very thin sheet caoutchouc, the surface applied to the roll having been previously rubbed with the caoutchouc solution to cause it to adhere firmly. The roll is then cut into proper lengths for stoppers, and the ends are covered with caoutchouc in a similar manner.

The combination of the shreds and small lumps of crude caoutchouc into a large block, from which a sheet may be cut, is effected by attrition and compression. In one method, the caoutchouc is first cleansed by being cut into small pieces, which are washed with water, and dried on hot iron trays. The pieces are then laminated by being passed between two iron rollers, and washed at the same time by a stream of water. This operation is repeated so long as the caoutchouc retains any foreign matters capable of being removed by washing.

The caoutchouc is then introduced into a strong iron cylinder, the interior of which is furnished with projecting spikes. The line of the axis of the cylinder is traversed by a strong shaft of wrought iron, which is also furnished with projecting spikes. By the revolutions of the iron shaft, the cylinder being fixed, the caoutchouc becomes kneaded, or "ground" (as termed by the workmen), evolves considerable heat from the rapid expansions and contractions which it suffers, and aggregates into a single elastic lump.

The kneading is completed in about two hours, and the caoutchouc is then squeezed into a compact cake by the action of a hydraulic press or a screw press. The mass must remain under the press until quite cold.

By another method, the preliminary washing and mamination are dispensed with, and the caoutchouc is washed by a stream of water admitted into the cylinder during the attrition. The water passes off through apertures in the bottom of the cylinder. After trituration for half an hour, the pieces become aggregated into a single mass, which is then transferred to another similar cylinder, where it is agitated dry, with a little quicklime. The temperature of the caoutchouc soon becomes very high, and steam and air are discharged in considerable quantity. After another trituration alone in a third cylinder for the purpose of condensing it into a homogeneous solid, the ball is agitated in a larger cylinder with several other similar balls, until they all become perfectly incorporated, when the mass is pressed into a cast-iron mould.

The block obtained by either of these methods is cut into small cakes and sheets by a straight steel blade made to vibrate rapidly in a horizontal plane. The sheets of caoutchouc are mostly employed in making tapes and threads of caoutchouc to be covered with cotton, silk, linen, &c. to form every variety of elastic tissue.*

Slabs formed of a mixture of caoutchouc and sand or saw-dust have been lately employed as a pavement,

* See an article by Dr. Ure on the caoutchouc manufacture in the *London Journal of Arts, &c.*, vol. xiii., Conjoined Series.

both for roads and for buildings exposed to wet, as a lining and top covering for walls, &c.

To make these slabs, the caoutchouc is reduced to a pasty state by attrition in a cylinder with a revolving axis, as already described; and when in that state, a quantity of slightly charred saw-dust is introduced into the cylinder, and intimately mixed with the pasty caoutchouc. As much saw-dust is introduced as the caoutchouc will take up without losing its adhesiveness. The mixture is then taken out of the cylinder and submitted to pressure in an iron mould; a quantity of coarse sand being applied to that part of the mould which is opposed to the part intended to form the upper surface of the block. The blocks remain in the mould under pressure until they are cold. For roads through which there is considerable traffic, the thickness of the slabs may be three inches; for footpaths, one inch; and for a covering for walls, a quarter of an inch. They may be placed on any convenient substratum, and are cemented together at their edges by the solution of caoutchouc in naphtha. Sand may be used instead of saw-dust in the composition of the slabs; but the latter is preferred by the patentee of this invention.

Caoutchouc was not introduced into Europe previous to the beginning of last century. Nothing was known of its origin except that it was a vegetable production, until the expedition of the French Academicians to South America, in 1735, in order to measure a degree of the meridian, when it was ascertained to be an inspissated juice, and an account of

the discovery was sent to the French Academy the following year by M. de la Condamine. In 1751 M. Fresnau also communicated some observations on the subject to the Academy, and the Memoirs of that body for the year 1768 contain an account of the properties of caoutchouc by M. Macquer.

The importation of this substance into Great Britain has now reached several hundred tons yearly, and is continually on the increase. Its importance as an article of commerce is such that some of the West Indian planters are said to make the *Iatropa elastica* the only object of their extensive cultivation.

BORAX, AND THE BORACIC LAGOONS.

§ I. History and Properties of Borax.—II. Boracic Acid.—III. Manufacture of Borax from Boracic Acid.

§ I. HISTORY AND PROPERTIES OF BORAX.

BORAX is a saline compound found native in great abundance in China, in the island of Ceylon, in certain lakes of South America, and near the mountains of Thibet in the East Indies. The substance is a combination of soda with a peculiar acid, first isolated by Homberg about the commencement of last century. The acid is now known to be a compound of oxygen with an elementary substance, to which the name of *boron* is applied: the acid itself is called *boracic acid*.*

Until the recent discovery of a more advantageous mode of obtaining borax, this salt was brought to Europe in considerable quantities from the East Indies, where it is found as an efflorescence on the soil, and also dissolved in the waters of certain lakes. It

* The history of borax may be traced back to a very early period. It was familiarly known to the Arabians by the name of *baurach*, the probable origin of its present designation. Baurach was a term, however, applied to carbonate of soda, the *nitrum* and *natron* of the ancients, which was found as an efflorescence on the soil. Borax and carbonate of soda resemble each other to a certain extent in being possessed of alkaline and detergent properties, but in most of their chemical characters these salts differ essentially. It is believed that borax is one of the substances described by Pliny under the name of *chrysocolla*, from

was imported in small dirty crystalline masses called *tincal*, or rough borax, which contain scarcely more than half their weight of pure borax, the remainder consisting chiefly of a peculiar saponaceous combination of soda with a fatty acid. The salt was never termed borax until purified.

For a long time the process of refining tincal was practised in Europe only at Venice, on which account the purified borax was called Venetian; but at length the enterprising Dutch made themselves masters of the process, and succeeded in completely engrossing the manufacture. Their mode of refining, which was long kept a profound secret, is similar in principle to that employed in the present day, and consisted in the application of lime, which formed an insoluble combination with the fatty acid of the saponaceous compound.

The following is one of the modern processes for refining tincal. The crude salt, being placed in proper pans, is covered with cold water to a height of two or three inches above its surface, and allowed to stand for some hours. Recently slaked lime is then added to the amount of one part to four hundred parts of tincal; the mixture is thoroughly stirred, allowed to stand for twelve hours, again strongly agitated, and the troubled supernatant liquid decanted.

the property attributed to the latter of facilitating the soldering of gold with other metals, which is possessed in an eminent degree by borax; but chrysocolla was a name also applied by Pliny to the green carbonate of copper or malachite.

Baurach is among the many chemical preparations, noticed by the Arabian, Geber, who lived in the eighth century. It was employed by him for one of the same purposes as it is at present, namely, to assist in reducing the oxides of certain metals to the metallic state.

The liquor is not thrown away, but preserved to wash the impure borax; the solid matters held in suspension being first separated by subsidence and decantation. The washing is continued with the same liquid, clarified by subsidence as often as applied, until it is no longer rendered turbid. In this way a great portion of the fatty matter may be washed away as an insoluble soap of lime. The salt thus purified is dissolved in two and a half parts of boiling water, and mixed with a solution of chloride of calcium containing two parts of that salt to one hundred parts of tincal. A precipitate is thereby produced, consisting chiefly of the insoluble soap of lime; the liquor is separated from the precipitate by filtration, and evaporated down to the density 1.14 or 1.16. It is then run off into crystallizing vessels, and cooled very gradually in order to obtain large crystals.

The preceding process has received various modifications; but as tincal is now no longer the European source of borax, an account of these is unnecessary.

Borax has a sweetish and alkaline taste, and changes certain vegetable colours in the same manner as an alkali. Notwithstanding its alkaline reaction, it is believed to contain two proportions of acid* to one of soda; but the acid characters of boracic acid are too feeble to neutralize completely the alkaline properties of the base. In this respect borax may be assimilated to the bicarbonates of the alkalies. The specific gravity of borax is 1.705. It is soluble in twelve parts of cold water, and in twice its weight of boiling water. The crystals of borax which are formed at

* It is doubtful whether the equivalent of boracic acid should be taken as thirty-five or twice that number.

common temperatures have the following composition:

One equivalent of soda	31	16.2
Two equivalents of (or one eq. ?) boracic acid	70	36.6
Ten equivalents of water	90	47.2
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One equivalent of borax	191	100.0

When exposed to a dry atmosphere at the ordinary temperature, this salt commonly effervesces slightly, and loses a portion of its water.* If moderately heated, it readily fuses, swells considerably from the escape of steam, and at a red heat becomes anhydrous.

If the heat has been insufficient to fuse the borax, it remains as a light white porous mass known as calcined borax.

When borax is crystallized from a solution the temperature of which is above 133° Fahr., it assumes a form different from the above crystals, and combines with a different proportion of water of crystallization, namely, five equivalents. The shape of these crystals is the regular octohedron. They contain

Soda	21.3
Boracic acid	47.9
Water	30.8
<hr/>	
100.0	

The specific gravity of this compound is 1.815.

From containing a smaller proportion of water than ordinary borax, this variety is preferred by braziers in soldering. It is usually distinguished as octohedral borax. The possibility of obtaining another borax with a still smaller proportion of water of crystallization, is a subject which well deserves the attention of the borax manufacturer.

* According to Mr. O. Sims, this salt does not effloresce if entirely free from carbonate of soda.

Anhydrous borax fuses when heated strongly, and forms a limpid and colourless glass, which is still capable of being dissolved in water. Like many other vitreous substances in a state of fusion, borax is capable of dissolving most metallic oxides, forming with several glasses of particular colours, from the nature of which the nature of the metallic oxide may often be determined.*

* The use of borax as a re-agent in analysis by the blow-pipe depends on this property. If a minute quantity of either of the oxides mentioned in the following table is added to a bead of borax fused on the end of a platinum wire bent in the form of a hook, and heated in the exterior blow-pipe flame, the bead acquires a well-marked colour, according to the nature of the oxide. In the exterior blow-pipe flame these colours are as follow :

Oxide of cobalt	Intense blue.
Oxide of manganese	Deep violet or amethyst.
Oxide of chromium	Reddish white hot, emerald-green when cold.
Black oxide of copper	Deep green.
Peroxide of uranium	Lemon-yellow,
Oxide of iron	Red while hot, faint yellowish-green when cold.
Oxide of nickel	Reddish white hot, light emerald when cold.
Oxide of antimony	Yellowish while hot, colourless when cold.

If the bead is brought into the interior flame of the blow-pipe, or the reducing flame, the colour produced by some metallic oxides wholly disappears ; but more frequently the bead passes from one colour to another. This is the case with most of the oxides mentioned in the preceding table. The colours of the beads in the interior flame are as follow :

Cobalt	Intense blue.
Manganese	Colourless.
Chromium	Emerald green.
Copper	Ruby red.
Uranium	Dark green.
Iron	Brownish-green.
Nickel	Grey from metallic nickel.
Antimony	Grey from metallic antimony.

On this property of dissolving metallic oxides is founded the use of borax to braziers, silversmiths, and others, in the soldering of metals; for which purpose, merely, about two tons of borax are consumed in Birmingham weekly.* When heated, with exposure to the air, most metals acquire a coating of oxide, which would, if allowed to remain, effectually prevent the perfect contact of two pieces. But if a little borax is sprinkled on the metal, the oxide is dissolved, and the access of air prevented by the fused salt; the surface is thus cleaned, and the liquid salt offers no impediment to the combination of the metal with the solder.

The most considerable consumption of borax at present is at the potteries, chiefly in the formation of a porcelain and earthenware glaze, an application dependent on the vitreous character of most combinations of this salt with metallic oxides and earthy bases. The particular composition of the borax glaze is varied at different potteries, but the essential constituents, besides borax, are felspar and soda. Nitre is sometimes added in small quantity, and a mixture of powdered flint-glass and flints is occasionally substituted for felspar. At a single pottery there is a consumption of from eighty to a hundred tons of borax per annum.

Borax also enters into the composition of some varieties of glass, and would be extensively used for that purpose, did its price permit. A glass recommended for optical purposes has been made with seven parts of red lead, two parts of calcined borax,

* Information supplied by Mr. Kurtz of Liverpool.

and three parts of ground quartz. The addition of a little borax to the materials for plate-glass and crown-glass has been recommended; but a large quantity seems to communicate an exfoliating property to the glass. The vitreous body of artificial gems called *strass* (from the name of its German inventor) is a kind of flint-glass, in most receipts for which borax is mentioned as an essential constituent. According to Dr. Shaw (Chem. Lectures), by fusing together four parts of borax and one part of fine white sand, a pure glass is formed, sufficiently hard to cut common glass like the diamond.

Borax is used to a large extent in assaying metallic ores to dissolve the mineral, and facilitate the reduction of the oxide by carbonaceous matters. It is eminently adapted for this purpose, as it forms fusible combinations, not only with bases, but also with silica.* An aqueous solution of borax has the remarkable property of dissolving shell-lac, affording a solution which may be employed as a kind of varnish. The proper proportions of the materials are five parts of borax and one of shell-lac.

§ II. BORACIC ACID.

When a solution of borax in water, nearly saturated at its boiling point, is mixed with a quantity of oil of vitriol equal to one fourth the weight of the borax, thin crystalline plates of boracic acid are

* See an account of some interesting experiments on the solvent power of fused borax by M. Berthier in his *Traité des Essais par la voie sèche*, t. i. p. 475, *et seq.*

deposited on the cooling of the solution. To purify the acid, it is first washed with cold water, in which it is but sparingly soluble, and then dissolved in boiling water, and made to crystallize afresh. The boracic acid thus obtained is sufficiently pure for most of the purposes to which it is applied, but it retains a trace of sulphuric acid, probably in a state of chemical combination. This small quantity of sulphuric acid may be separated, if necessary, by fusing the boracic acid in a platinum crucible at a red heat.

Boracic acid is inodorous, and has a weak taste scarcely at all acid. In aqueous solution it is one of the feeblest of acids; instead of changing the colour of blue litmus to that clear red produced by the strong acids, it imparts a wine-red tint similar to what is communicated by carbonic acid, and its combinations with the alkalies retain alkaline characters, though they contain an excess of boracic acid. But at a red heat this acid seems to possess a very powerful affinity for bases; it then displaces the greater number of those acids which are more volatile than itself, from their saline combinations, an effect referable to the great fixedness of boracic acid when in the anhydrous condition. When unmixed with any volatile substances, boracic acid is perfectly fixed at a bright red or even white heat; but it is remarkable, that in the presence of the vapour of water or of alcohol this acid is certainly capable of volatilizing to a considerable extent, and may be condensed in small sparkling crystals. In the original process for the preparation of this acid, instead of crystallizing it from a solution of borax mixed with oil of vitriol, such a mixture was distilled in a retort, in the neck

of which the acid was collected in small crystals. The acid prepared by this and similar processes was long ago employed in medicine under the names of *Homborg's sedative salt*, *Sal volatile narcoticum*, *Flores boracis*, *Sal album alchymistarum*, &c. Neumann seems to have been the first who prepared boracic acid without distillation.

Anhydrous boracic acid melts under a red heat into a colourless and transparent glass, which is still soluble in water. The specific gravity of the vitrified acid is 1.83, and of the crystallized acid 1.48. The crystallized acid requires 25.66 times its weight of water at 60° for its solution, but only 2.97 times at 212° (Berzelius). Boracic acid is soluble in alcohol, and the solution when set on fire burns with a fine green flame; a property which affords an excellent test for the presence of this acid. The alcoholic solution of boracic acid communicates a brown colour to yellow turmeric paper, like an alkali, and the colour becomes deeper as the alcohol evaporates.

The constitution of boracic acid was first ascertained by Sir H. Davy in the year 1807. By exposing it to the action of a powerful galvanic battery he obtained a small quantity of a greenish-brown powder, which burned vividly when heated in atmospheric air or oxygen gas, and then returned to the state of boracic acid. Boracic acid is hence viewed as a combination of oxygen with the above substance, which is regarded as an element, and called *boron*. MM. Gay-Lussac and Thenard prepared boron by heating boracic acid with potassium, when the latter sepa-

rates oxygen from the former, and sets the boron at liberty. The easiest method of preparing this substance is to decompose by means of potassium the salt called borofluoride of potassium, which is a combination of fluoride of potassium with fluoride of boron. When that substance is heated with potassium, the fluoride of boron is decomposed, with production of fluoride of potassium and consequent liberation of boron.

Boron is a tasteless and inodorous substance, insoluble in water, alcohol, ether, and oils. It may be heated *in vacuo*, or in gases which do not combine with it, without undergoing any change, except a slight deepening of colour and increase of density. It is devoid of the metallic lustre, and is a non-conductor of electricity. At common temperatures it undergoes no change by exposure to atmospheric air or oxygen; but if heated to 600° Fahr., it burns with brilliant scintillations, and forms boracic acid, which is the only known combination of boron and oxygen. The generally received equivalent number of boron is 11. Its symbol is B.

When boron passes into the state of boracic acid, it unites with a quantity of oxygen equal to 68.6 per cent. of the product, which is considered to contain three equivalents of oxygen and one of boron, thus ($B + O_3$); in which case, the equivalent of anhydrous boracic acid is 35, or one equivalent of boron = 11 + three equivalents of oxygen = 24. The boracic acid deposited in crystals from an aqueous solution is a hydrate containing 43.5 per cent., or three equivalents of water.

Boracic acid is found in nature not only in combination with soda, and to a small extent with some earthy bases, but likewise in a free state, constituting in that form a very abundant, interesting, and highly important volcanic product. It is found in the Lipari Islands, but most abundantly in the hot springs of a small district in Tuscany, the boracic lagoons of which have now become the common European source of borax. These lagoons or lakes may be ranked among the wonders of the age, and are unique in Europe, if not in the world. They are situated on the sides of hills, and are supplied with water by the condensation in them of volcanic vapours or soffioni, highly charged with free boracic acid, together with borate and sulphate of ammonia, and several other saline matters. The soil surrounding these beds of hot water is covered with a saline efflorescence, consisting chiefly of boracic acid, but likewise containing, in smaller proportion, ammoniacal salts, borate and sulphate of alumina, and persulphate of iron.

The presence of boracic acid in these vapours was first announced by Hoefer in the year 1776, and the manufacture of borax from this source was suggested about the same time by Mascagni. It was not attempted, however, till several years afterwards. Some experiments performed by Professor Gazzeri, in 1807, tended to shew that the quantity of boracic acid contained in the lagoons was too small to render them an advantageous source of borax; and this was afterwards fully proved to be the case, when the water, as found in the lagoons, was evaporated by heat obtained artificially in the ordinary manner. A

succession of adventurers had in this way produced a considerable quantity of boracic acid, but the cost of fuel for the evaporation was so great as to leave but little profit; so that the lagoons, now a source of wealth, "more valuable, perhaps, and certainly less capricious, than any mine of silver that Mexico or Peru possesses,"* were formerly considered all but worthless. Important improvements were, however, gradually introduced; one of the earliest of which was the subjecting the same quantity of water to successive impregnations of vapour, so as to increase the proportion of boracic acid. This improvement was made by Signor Ciaschi, who perished miserably in 1816, from having fallen into a lagoon of his own excavation. In the following year the lagoons came into the possession of their present spirited proprietor, the Count de Pomerance (better known as M. Larderelle), who conceived the happy idea of abandoning the use of wood-fuel in the evaporation of the waters, and applying the heat of the superabundant vapour itself. This is the grand improvement which has given the boracic lagoons of Tuscany their present importance.

Without the assistance of fuel, machines, or chemical materials, a produce of seven hundred and fifty thousand kilogrammes (a little more than one million six hundred and fifty thousand pounds) of boracic acid is obtained yearly with an evaporation of more than eighty millions of kilogrammes of water; and all this is effected merely by giving a proper direction to the vapours of the soffioni themselves.

For the following account of the lagoons I am

* Dr. Bowring.

indebted to Dr. Bowring's Parliamentary Report on the Statistics of Tuscany, and to a description of the process of manufacture in a paper by M. Payen in the *Annales de Chimie et de Physique*, tom. i. 3^{me} série, p. 247. An abstract of Dr. Bowring's report appeared in the Philosophical Magazine for July 1839, and a translation of M. Payen's paper in No. 8 of the Chemical Gazette (Feb. 15th, 1843).

"As you approach the lagoons," observes Dr. Bowring, "the earth seems to pour out boiling water, as if from volcanoes of various sizes, in a variety of soil, but principally of chalk and sand. The heat in the immediate adjacency is intolerable, and you are drenched by the vapour, which impregnates the atmosphere with a strong and somewhat sulphureous smell. The whole scene is one of terrible violence and confusion—the noisy outbreak of the boiling element—the rugged and agitated surface—the volumes of vapour—the impregnated atmosphere—the rush of waters—among bleak and solitary mountains.

"The ground, which burns and shakes beneath your feet, is covered with beautiful crystallizations of sulphur and other minerals. Its character beneath the surface at Monte-Cerboli is that of a black marl streaked with chalk, giving it at a short distance the appearance of variegated marble."

The place was formerly regarded by the peasants as the entrance of hell; they never passed by the spot without terror, counting their beads and praying for the protection of the Virgin. Besides the superstitious dread entertained of the lagoons, their frightful appearance and foetid smell, arising from

the evolution of sulphuretted hydrogen gas, made them to be regarded as public nuisances, and rendered fruitless all attempts on the part of the landlords to improve the surrounding country. But since the lagoons have been turned to profitable account, a great improvement has taken place in the cultivation, and increase in the value, of the neighbouring soil. The health of the workmen, who live constantly on the spot, is in general good.

The lagoons themselves are situated on a gently sloping ground, with the manufactories at the bottom, a short distance from each other. The number of establishments is nine; of which the principal are Larderello, Monte-Cerboli, Monte-Rotundo, Sasso, Lerrazano, and Castel-Nuovo.

With some slight modifications, the routine of the operations is the same in each of the nine manufactories. A sufficiently precise idea of the process may be obtained with the assistance of the annexed engraving, which represents an imaginary section of the surface of the earth through the lagoons. This cut is an accompaniment to the paper of M. Payen before alluded to.

The lagoons consist of rude circular basins, partly excavated and partly built, situated immediately over one or more of the fissures through which the soffioni burst. They are arranged at different elevations, and connected with each other by canals to allow of the transference of the liquid from a higher to a lower lagoon. A small lake is formed in the highest of these basins by introducing the water of some adjacent mountain stream. The water is soon heated

Fig. 30.



to the boiling point, and kept in perpetual agitation by the passage of the hot vapours, which deposit most of their boracic acid in the lagoon, and afterwards rise into the air as whitish clouds. The vapours produce boracic acid only when they burst with a fierce explosion.

After having remained in the most elevated lagoon, *a*, for twenty-four hours, the water is allowed to descend through the canal *c* (by opening a plug in the canal) to the second lagoon *b*, where it is subjected during twenty-four hours to another impregnation. It is then passed on to the third lagoon, and so on successively, until it is arrived at the lowest

receptacle, having thus passed through from five to eight. With all these impregnations, the quantity of boracic acid in the water of the last lagoon scarcely exceeds one-half per cent. As the liquid is drawn off from one basin, it is immediately replaced by that contained in the next above.

When the solution has remained a sufficient length of time in the lowest lagoon *d*, it is transferred to a reservoir or cistern *e*, six metres (about twenty feet) square, and one metre (about three feet four inches) deep; from whence, after a few hours' rest to deposit some sedimentary matter, it is decanted either into a second reservoir *f*, or into the evaporating pans.

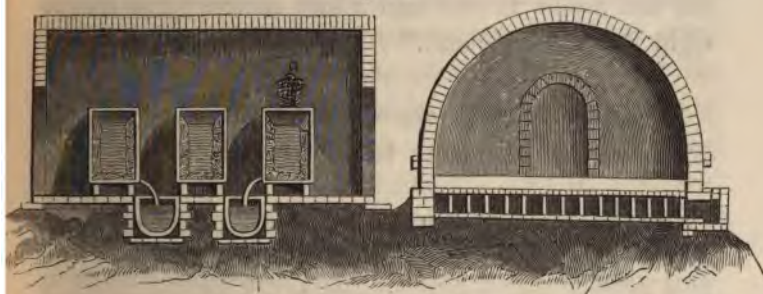
The arrangement for evaporating consists of two batteries, each composed of seven leaden pans, *g g*, 2.90 metres in breadth, and 0.35 metre in depth. The pans, which are arranged at different levels, are supported by strong wooden rafters above the masonry, so as to allow the passage of the vapour of some soffioni underneath as through a drain. The vapour enters at the bottom of the lowest pan, and passing under all the others in succession, the excess is at last given off outside the manufactory.

The first four pans of a series of seven are filled with liquid from the reservoir *f*, and the evaporation of the boracic solution is carried on here during twenty-four hours. The solution thus concentrated is passed on to the remaining pans by means of siphons, each pan being replenished when the liquor is withdrawn from that next above it, and the highest from the reservoir. In the last two pans the evaporation is carried so far that the liquid crystallizes when transferred into vessels arranged for the pur-

pose, which are wooden tubs lined with lead. The specific gravity of the crystallizing solution is from 1.072 to 1.080, at a temperature of from 173° to 176° Fahr. When the crystallization is complete, the mother-liquor is withdrawn and returned to the last two pans to be evaporated, together with another quantity of the solution; and the crystallized acid is placed in baskets to drain. It is then removed to the drying-rooms and spread on the floor in layers, which are occasionally turned. After two or three hours, or when it feels tolerably dry, the acid is packed up in casks, and sent to Leghorn for exportation.

The drying-room, represented in section at fig. 31,

Fig. 31.



is also heated by the soffioni, being constructed with a double floor for that purpose, through which the vapour is made to circulate. It is built of brick.

A battery of fourteen pans affords daily about ninety kilogrammes of saleable boracic acid. The whole product of the nine establishments varies from seven to nine thousand pounds (of twelve ounces) daily. The state of the weather has some influence on the amount of the product. In bright and clear weather, both

in winter and in summer, the vapours are less dense, but the quantity of boracic acid deposited is greater. Increased vapours indicate unfavourable change of weather; and the lagoons act as infallible barometers to the neighbourhood, even at a great distance, serving to regulate the proceedings of the peasantry in their agricultural pursuits. (Dr. Bowring.)

The different manufactories contain from one to five batteries, each comprising fourteen or sixteen evaporating pans. The number of lagoons to each establishment varies from three to twenty-five. The largest lagoons are from fifteen to twenty metres (from forty-nine feet to sixty-six feet nearly) in diameter, and the smallest from four to five metres (thirteen feet to sixteen feet and a half); their depth varies from one and a half to two and a half metres (five feet to eight feet three inches).*

Before describing the process of converting the crude boracic acid into borax, it will be proper to

* "It appears to me," observes Dr. Bowring, "that the powers and riches of these extraordinary districts remain yet to be fully developed. They exhibit an immense number of mighty steam-engines furnished by nature at no cost, and applicable to the production of an infinite variety of objects. In the progress of time this vast machinery of heat and force will probably become the moving central point of extensive manufacturing establishments. The steam, which has been so ingeniously applied to the concentration and evaporation of the boracic acid, will probably hereafter, instead of wasting itself in the air, be employed to move large engines, which will be directed to the infinite variety of production which engages the attention of labouring and intelligent artisans; and thus, in the course of time, there can be little doubt, that these lagoons, which were fled from as objects of danger and terror by uninstructed man, will gather around them a large intelligent population, and become sources of prosperity to innumerable individuals throughout endless ages."

advert to M. Payen's researches on the nature of the substances which accompany the boracic acid, and his theoretical views of the origin of the products.

The vapours are not entirely condensable; a gas is given off, which on examination proved to be a mixture of carbonic acid, nitrogen, oxygen, and sulphuretted hydrogen in the following proportions:

Carbonic acid	57.30
Nitrogen	34.81
Oxygen	6.57
Sulphuretted hydrogen	1.32
	<hr/>
	100.00

The condensable products and the substances brought up mechanically by the powerful current of vapour, are the following:—water, clay, sulphates of lime, ammonia, alumina, and iron; hydrochloric acid; organic substances possessing a *marine* smell (probably like that of sea-weed), sulphur, and the merest trace of boracic acid. The temperature of the vapours was found to vary between 206° and 212° Fahr. (97° and 100° Cent.). No boracic acid could be obtained by condensing the vapours of the soffioni in large and long tubes; the product was only an acidulated water containing no boracic acid. To obtain the latter, it seems essential that the vapour should be brought into contact with water; and it is often observed that a portion of the water absorbed, when a lagoon is filled, is subsequently ejected by the vapour. Thus the production of boracic acid, or rather the arrival of the acid to the surface of the earth, seems to depend on the introduction of water through the fissures.

From these observations M. Payen draws the fol-

lowing theoretical conclusions: All the phenomena would be perfectly intelligible, if it be admitted that the water of the sea, penetrating through some fissure to a great depth, may have its temperature raised to a high degree, and find in the soffioni an exit for its vapours. The boracic acid would then be derived from deposits of that substance, through which the vapours and the projected water rush; and the sulphuretted hydrogen from the decomposition, by means of boracic acid, of sulphurets formed by the reaction of the organic matter contained in the water on the sulphates also present in the water.

These facts admit, however, of a more chemical explanation. "Admitting with M. Dumas," observes M. Payen, "that a deposit of sulphuret of boron, situated at a great depth, came into contact with sea-water, a lively action would take place, from which would result boracic acid, sulphuretted hydrogen, a high temperature which would carry off these products with the water, hydrochloric acid arising from the decomposition of earthy chlorides, and ammonia produced by the organic matters. If the action take place at a little distance from a calcareous mass, the boracic acid conveyed in the current of vapour would decompose the carbonate of lime, and the equivalent of carbonic acid would mix with the other gases; at a certain distance the sublimed boracic acid might form deposits, and according as the water of the lagoons descended to this point, or not, the return current would carry up with it boracic acid, or pass without volatilizing the acid.

"The air furnished by the sea-water, or other source, would enter the fissures, and determine, in

the presence of sulphuretted hydrogen, the formation of sulphuric acid. This, in its turn, would produce sulphates of lime, of ammonia, of alumina, and of iron, taking the lime from the calcareous mass, the ammonia from the vapours, the alumina and iron from the clay. These different salts, which are formed or which dissolve in the waters near the surface of the soil, explain the disintegration of the latter. The appearance of sulphur, and the presence of a little oxygen, which accompany the various substances contained in the soffioni and in the troubled waters of the lagoons, would proceed from the accidental introduction of air."*

§ III. MANUFACTURE OF BORAX FROM BORACIC ACID.

As sent out of the establishments, the boracic acid is commonly far from being a pure substance, and the proportion of impurities, moreover, is said to be continually on the increase. Formerly the product contained from 90 to 92 per cent. of pure crystallized boracic acid; at present, the proportion varies

* M. Payen suggests that a portion of the boracic acid may be produced by the re-action of sulphuric acid, so abundant in masses of disintegrated soil, on anteriorly formed borate of lime.

Neither of the above hypotheses presents a satisfactory explanation of the origin of the ammonia which always accompanies the native boracic acid in considerable quantity; the organic matters which would be introduced by the sea-water being far too small in quantity to be admitted as the probable source of the ammonia. It is suggested by Mr. Balmain that this body may be produced by the decomposition, by means of water, of *athogen*, or some analogous compound of boron and nitrogen, which, when heated with water, becomes decomposed, with formation of boracic and free ammonia; the oxygen of the water having united with the boron, and the hydrogen of the water with nitrogen.

between 74 and 83 per cent. This is attributed to the progressive alteration of the disintegrated strata by the currents of vapours and the infiltrations of water.

The crude acid has been subjected to a complete analysis by M. Wittstein, in which he obtained the following results (Buchner's *Repertorium*, xxii. 145):

Crystallized boracic acid, ($\text{BO}_3 + 3 \text{HO}$)	76.494
Sulphate of manganese	a trace
Persulphate of iron	0.365
Sulphate of alumina320
Sulphate of lime	1.018
Sulphate of magnesia	2.632
Sulphate of ammonia	8.508
Sulphate of soda917
Sulphate of potash369
Muriate of ammonia298
Sulphuric acid in combination with boracic acid	1.322
Silicic acid	1.200
Water of crystallization of the salts above	6.557
Organic matters	a trace
	<hr/> 100.000

It has been a matter of surprise that no steps are taken to purify the acid on the spot, as a very considerable expenditure in packages, freight, &c., might thereby be avoided. The impurities may be removed to a great extent by subjecting the drained acid to a strong pressure, and purifying the residue by washing; and one half of the water contained in the crystallized acid might be expelled by a prolonged desiccation at 212° , whereby the proportion of dry or real acid in the impure material would be increased from 56 to 72 per cent.

But some borax manufacturers consider a given

weight of the pure acid to be less valuable than as much crude acid as contains an equal quantity of the pure acid, in consequence of the large proportion of sulphate of ammonia contained in the crude acid (sometimes fourteen per cent.), which may be made available in the manufacture of ammoniacal salts. With this view, the crude acid is first washed with cold water (whereby it loses from five to twenty per cent. of its weight), and the washings are concentrated by evaporation, on which they afford a large quantity of a well crystallized salt, which is the double sulphate of magnesia and ammonia. Very little boracic acid is mixed with these crystals; but the mother-liquor is a strong solution of boracic acid, which does not afford crystals, though its density is very high.

The process for making borax from the crude acid, as carried on successfully in M. Payen's works at Paris, is the following:* it differs slightly in its details from the method pursued in this country.

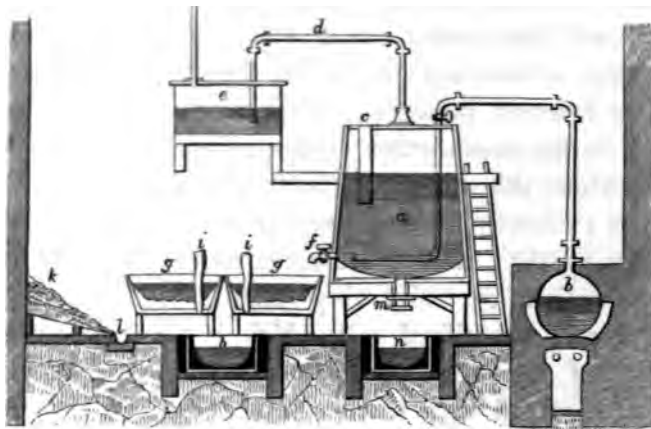
The materials operated on are one thousand kilogrammes of the crude acid, twelve hundred kilogrammes of crystallized carbonate of soda,† or the equivalent quantity of dry carbonate, or of the *soda-ash* of commerce, and about two thousand kilogrammes of water, minus the quantity which may be furnished by the mother-liquor of a preceding operation‡ and that introduced by the condensation

* Information derived from a paper on the subject, by M. Payen, in the *Ann. de Ch. et de Ph.* t. ii., 1841, p. 322.

† At an extensive borax work in this country, the proportions of soda and acid which are employed, are, eight parts of unwashed acid, and ten parts of soda-crystals, or the equivalent quantity in soda-ash.

‡ The regular addition of the mother-liquor of one operation to the

Fig. 32.



of the steam applied as a source of heat. The carbonate of soda is first dissolved in a vat *a*, fig. 32, lined with lead and heated by steam from the boiler *b*. The pipe which conveys the steam leads nearly to the bottom of the vat, where it is bent into a horizontal circle and pierced with holes to emit the steam. When the carbonate is dissolved and the temperature of the solution raised to near 212° , the boracic acid is added in quantities of from four to five kilogrammes at a time through the pipe *c*, and the carbonic acid and other gases then evolved are conducted by the tube *d*, attached to the cover of the vat, into a condenser *e*, containing sulphuric acid. The object of passing the gas into sulphuric acid is to collect some ammonia which is disengaged

solution of borax made in the next, is by no means advisable, as the quantity of impurities must then be continually on the increase. The extraction of the whole of the borax from the mother-liquors requires a tedious and somewhat complicated process.

in the state of carbonate. When all the boracic acid has been introduced, the solution ought to have the specific gravity 1.17 (21° of Baumé's hydrometer). Its boiling point is then about 221° Fahr. (105° Cent.).

The supply of steam is now cut off, the opening, *c*, covered, and the solution allowed to stand for ten or twelve hours. A deposit takes place, and the clear supernatant liquid is withdrawn by the stop-cock *f*, and conducted into crystallizing pans *g g*. These vessels are made of wood lined with thick sheet-lead. Their depth is about fifty centimetres (very near twenty inches).

When the crystallization is complete, the mother-liquors are conducted into the cast-iron trough *h*, placed below the evaporating pans: *i i* are wooden plugs encased in lead to be withdrawn for that purpose. The impure crystals of borax are detached from the pans, and set to drain on an inclined plane *k*, the floor of which is of lead: the drainings are collected in the gutter *l*.*

After the liquid in the vat *a* is decanted, the deposit is withdrawn by the pipe *m*, and received into the cast-iron trough *n*.

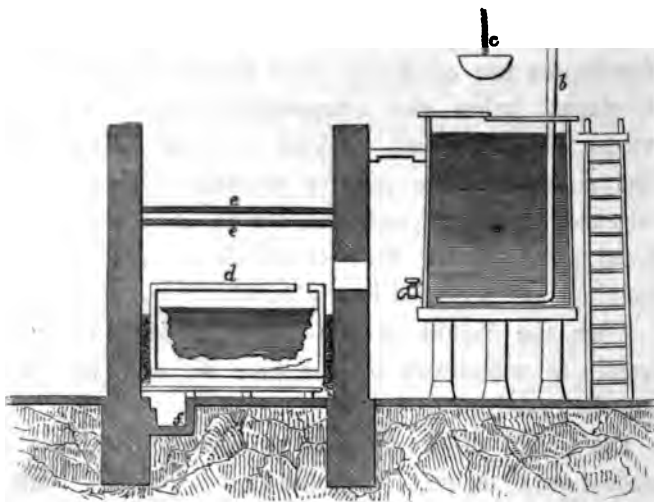
The object of the refining processes to which the crude borax is next subjected is not only the purification of the salt, but the formation of large and hard crystals. The small soft crystals which are procured from a solution of borax on the small scale

* These drainings, and the liquor collected in *h*, contain a quantity of carbonate and sulphate of soda, together with a little borax; by evaporating the liquid and calcining the residue with chalk and coal, the sulphate becomes converted into carbonate, but the greater part of the borax remains without alteration.

would hardly meet with a purchaser. Such were the crystals obtained in the first attempts to procure borax from the native acid for commercial purposes; but, though quite pure, their appearance formed a serious obstacle to their sale, as it was generally believed that the smallness of the crystals arose from the presence of impurities.

To procure crystals fit for the market, M. Payen proceeds in the following manner. The construction of the necessary apparatus may be understood with the assistance of the annexed cut: *a*, is the vat in

Fig. 33.



which the borax is redissolved; it is lined with lead, and is of sufficient capacity to contain a solution of nine thousand kilogrammes (nearly nine tons) of borax. The solution is effected with the assistance of heat derived from steam introduced by the leaden pipe *b* to the bottom of the vat.

The crude borax, and the small crystals of previous refinings, are placed in a basket made of iron rods *c*, suspended over the vat by a chain and pulleys. The vat being nearly filled with water, the basket is lowered so as to bring it immediately under the surface of the water; the borax is thus dissolved, and the sinking of the dense liquid to the bottom establishes currents in the liquid, which facilitate the solution of the remainder, and render any other agitation unnecessary.

For each quintal (1cwt. 3qrs. 25lbs.) of borax, about eight kilogrammes (between seventeen and eighteen pounds) of crystallized carbonate of soda are added to the vat, and the solution is brought to the specific gravity of 1.17 (21° Baumé). It is then transferred while boiling to the crystallizing vessel *d*, which together with its cover is lined with lead. Proper precautions must be adopted to preserve the crystallizing vat in a tranquil state, and to prevent a rapid reduction of its temperature. With the latter object it is surmounted with a double ceiling *e e*, the space between which and the vat is filled with charcoal powder, the top of the vat being covered with two or three pieces of thick woollen cloth. Underneath the vat is a pavement of flag-stones, or smooth bricks, having a gutter which leads into a small reservoir *f*. This serves to collect any droppings from defects in the soldering of the vat.

From twenty-five to thirty days, according to the external temperature, are required to complete the crystallization. Its progress may be ascertained by the temperature of the liquid. When between 77°

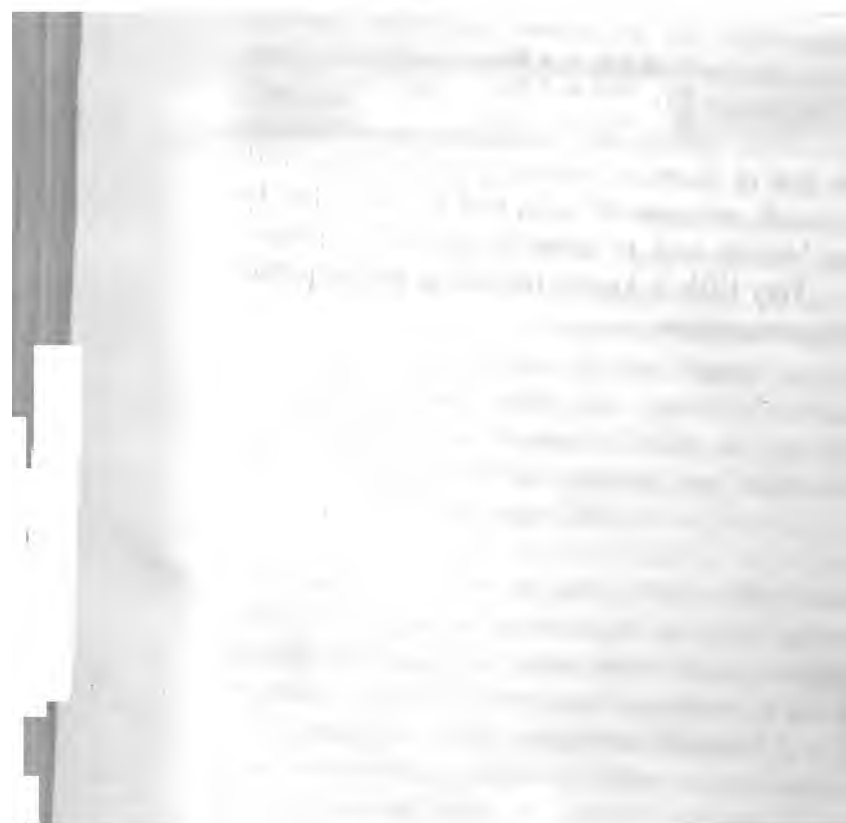
and 86° Fahr. (25° and 30° Cent.), the crystallization may be considered complete. The mother-liquor is then rapidly withdrawn by means of a large siphon, and the liquid which remains between the summits of the crystals imbibed by a sponge. The cover of the vat is replaced, and the crystalline mass is allowed to stand for five or six hours, so that its temperature may be gradually reduced to that of the external air. The crystals are then detached and assorted for the market. To procure borax in the octohedral form (see page 264), the solution of the crude salt should be made of the specific gravity 1.261 (30° Baumé), at the temperature of 212°, before being set to crystallize. The deposition of octohedral borax commences when the temperature of the solution falls to 174° Fahr. (79° Cent.), and terminates at the temperature of 133° Fahr. (56° Cent.). When at the latter temperature, the mother-liquor should be instantly withdrawn by a siphon to prevent the crystallization of ordinary prismatic borax. The liquor gives an abundant deposit of the latter applicable to several processes in which the salt is used.

Another method of preparing borax from the native boracic acid is by calcining a mixture of the latter (after being washed with water) with nitrate of soda. This process may be conducted very economically, provided the nitrous acid disengaged as gas through the decomposition of the nitric acid of the nitrate of soda be made available in the preparation of oxalic acid from sugar, or some other important manufacturing process. But it is difficult to find a material well adapted for the vessel to contain the

mixture, as siliceous substances are acted on by fused soda and borax with great facility; and an iron vessel would become rapidly corroded by nitrous acid.

The most economical process for preparing borax from boracic acid is the following, for which a patent has been recently obtained by Mr. Charles M. Sautter (May 1843). About 38 parts by weight of pure crystallized boracic acid ($3\text{HO} + \text{BO}_3$, or else a corresponding quantity of the washed native acid) are finely sifted and intimately mixed with about 45 parts by weight of powdered crystallized carbonate of soda ($\text{NaO}, \text{CO}_2 + 10\text{HO}$), and the mixture is placed upon wooden planks in layers of about one inch thick, in a room heated to any temperature between 90° and 115° Fahr. In the course of from twenty-four to thirty-six hours, the mass being occasionally stirred, the whole of the boracic acid and soda will have combined to form borax, the carbonic acid and superabundant water being expelled. The product thus obtained is fully adapted to all the applications of ordinary borax; but being in a granular state and not perfectly white, it will not, in all probability, meet with an extensive sale, at least for a few years hence.

Borax is sometimes sophisticated with common salt, and occasionally with alum. The presence of the former is easily detected by adding a few drops of a solution of nitrate of silver, which would afford a white curdy precipitate of chloride of silver, insoluble in nitric acid if the smallest quantity of common salt is present. The presence of alum in the borax may be detected by ammonia, which gives,



SOAP.

§ I. General principles of Soap-making Processes.—II. Materials employed in Soap-making.—III. Manufacture of Hard Soaps.—IV. Manufacture of Soft Soap.

§ I. GENERAL PRINCIPLES OF SOAP-MAKING PROCESSES.

As a generic term, *soap* is sometimes used to denote all kinds of combinations of unctuous matters with bases; whether alkalies, as potash and soda; earths, as lime and magnesia; or oxides of metals proper, as oxide of lead and oxide of zinc. This extended meaning of the term is hardly recognized, however, in common language; a soap being usually considered a compound of an unctuous substance with either potash or soda.

Though made by mixing an oil or a fat with an alkali, soap is not to be considered as a direct combination of the oil or fat, as a whole, with the alkali. When liberated from its combination with the base, by applying a strong acid, the oil is found to be altered in properties, being more soluble in alcohol and more easily saponified than before, and to have experienced an alteration in composition. This substance is capable of combining as a whole with a base to form a soap; but the original oil or fat contains another constituent besides the oil or fat capable of being eliminated from the soap by a strong acid.

In the course of an extended chemical examination of fixed oils and soaps, which occupied about fourteen years, M. Chevreul discovered that nearly all fixed oils and fats contain always two, and generally three, distinct compounds, united in the most various proportions. One of these, liquid at ordinary temperatures, has been named *oleine*; the other two, which are solid, but differ in fusibility, are named *stearine* and *margarine*. M. Chevreul also ascertained that each of these bodies contains an organic base,* soluble in water, named *glycerine* or *oxide of glycerule*, in combination with an unctuous substance, possessed of the essential characters of an acid. The acid constituent in each of the three fatty principles is peculiar, but the glycerine is common to them all. The acid in *oleine* is termed *oleic acid*; that in *stearine*, *stearic acid*; and that in *margarine*, *margaric acid*. *Oleine*, *stearine*, and *margarine* have therefore a saline constitution, and may be respectively regarded as the oleate, stearate, and margarate of glycerine.†

These fatty principles, when brought into contact with a free alkali, oxide of lead, or oxide of zinc, in the presence of water become decomposed; their acids leave the glycerine to unite with the alkali or metallic oxide (which are more powerful

* By an organic base is meant a substance capable of uniting with acids to form, in most cases, a neutral compound, like potash, soda, and other metallic oxides; but not derived, as these are, from the mineral kingdom.

† It is uncertain, however, whether the glycerine actually pre-exists as such in the oil, or is merely the product of the action of the base on the oil. The question is one of no practical importance whatever, since the oil is decomposable in this manner by very feeble bases.

bases than glycerine), forming, in the case of an alkali, a *soluble soap*, and in the cases of oxide of lead and oxide of zinc, *insoluble plasters*. When mixed with a solution of oxalic, tartaric, or other tolerably strong acid, these compounds are decomposed; their bases unite with the acid to form oxalates, tartrates, &c., while their oily acid is set at liberty, but in combination with a certain proportion of water. The glycerine liberated from the oleine, stearine, &c., by the action of an alkaline solution, is also in chemical combination with a definite proportion of water; and this body has not yet been obtained in the anhydrous state, as it is supposed to exist in the original oil. Hence the united weights of the fatty acid and glycerine obtained in this manner exceed the weight of the oil from which they were originally produced.

By far the greater number of fixed oils, both vegetable and animal, contain, when pure, no other constituent than oleine, stearine, and margarine; a few, however, among which is palm-oil, contain, in the place of one or more of these bodies, a peculiar fatty principle, quite analogous in its chemical constitution to oleine, &c., being a compound of glycerine with a peculiar fatty acid.

Soaps are divided into two kinds, *hard* and *soft*, differing from one another in the materials from which they are produced. Hard soaps are made from fats or vegetable fat-oils* and soda; for soft soaps, the oleaginous material is chiefly a fish oil or a vegetable drying oil, and the base potash. Hard soaps may

* Fat oils are those which do not, like drying oils, become converted into a dry resinous substance on exposure to the air.

be made, however, with potash, provided a solid fat is employed; but soda soaps are invariably harder than potash soaps, the unctuous material being the same. Of the hard soaps of commerce, those made with oils (excepting palm-oil) are mixtures of oleate and margarate of soda, with very little, if any, stearate; those made with animal fats are mixtures of oleate, stearate, and margarate of soda. On the Continent, in making hard soaps, potash is frequently introduced in the place of a portion of the soda.

Stearate of soda, which may be regarded as the type of hard soaps, is scarcely at all altered by contact with ten times its weight of water; but stearate of potash, placed in the same circumstances, forms a thick paste, or a viscid solution. In these respects, the margarates of potash and soda closely resemble the corresponding stearates. Oleate of soda, however, dissolves completely in ten times its weight of water, and oleate of potash in four times; the latter forms a jelly with twice its weight of water, and is so attractive of moisture, that one hundred parts, when exposed to a humid atmosphere, become increased merely by the absorption of water to two hundred and sixty-two parts (Liebig). Hence the harder and less soluble soaps contain more stearate and margarate, and less oleate, than the corresponding softer and more soluble soaps.

The quantity of pure, dry alkali required for the saponification of different kinds of oils and fats varies from about ten to fourteen parts of soda, and from fifteen to twenty parts of potash, for one hundred parts of the oil or fat. It is usual, however, to introduce a certain excess of alkali, in order to fa-

cilitate the separation of the soap from the mother-liquor; soap being insoluble in an alkaline solution of a certain strength. If no more alkali is introduced than the quantity exactly necessary for saponification, the action goes on slowly, and the soap remains dissolved in the liquor so long as the latter is hot; on cooling, the whole congeals to a gelatinous translucent mass. But if the alkali is present in a certain excess, or in a certain degree of concentration, or if some common salt is added to the mixture, the soap becomes insoluble and rises to the surface. This peculiar comportment of soda soap towards a solution of common salt and a strong alkaline ley is of great importance in the manufacture of soap, for on it depends the freedom of the soap from free alkali and glycerine, and also its proportion of water.

If a fat oil is boiled for a considerable time with one-half the quantity of solution of potash or soda necessary for its complete saponification, the whole of the oil dissolves when the mixture attains a certain state of concentration. Only one-half of the oil, however, is properly saponified, and the soap thus formed is the solvent of the other half. If diluted with water and boiled, this combination deposits a white fat, which is an intimate mixture of undecomposed oil and bimargarate and binoleate of potash or soda, which salts may be separated from the oil by the action of boiling alcohol (Berzelius). The utility of soap as a detergent agent depends principally on its property of rendering unctuous matters soluble in, or miscible with water, without exerting any corrosive action. A weak solution of

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The quantity of pure, dry alkali required for the saponification of different kinds of oils and fats varies from about ten to fourteen parts of soda, and from fifteen to twenty parts of potash, for one hundred parts of the oil or fat. It is usual, however, to introduce a certain excess of alkali, in order to

a caustic alkali would act more powerfully as a detergent, but it would at the same time tend to corrode the organic matters with which it is placed in contact. Soap acts, however, only by virtue of its alkali; a portion of which combines with the greasy matters to be removed by washing, the remaining alkali forming with the whole of the fatty acids a bistearate, bimargarate, and binoleate.

Ammonia is not so well adapted for saponifying oils as the fixed alkalies. If the emulsion obtained by agitating solution of ammonia with a fixed oil is mixed soon after being prepared with a dilute acid to neutralize the ammonia, or exposed to the air for the alkali to become dissipated by evaporation, the oil is reproduced in its original state; which shews that it had not been resolved by the ammonia into glycerine and the fatty acids. But if the emulsion is preserved for several months in a closed vessel, a true ammoniacal soap is produced.

Lime, barytes, magnesia, oxide of lead, and oxide of zinc, also saponify oils and fats in the presence of water with more or less facility. The action is in all cases accelerated by applying heat to the mixture. Glycerine is liberated and dissolved by the water, but the compounds of the fatty acids with these bases are insoluble.

The curdy precipitate which is produced when a soluble soap of any kind is mixed with common hard water, is an insoluble soap of lime, formed through the mutual decomposition of the carbonate or sulphate of lime in the water and the soap. The oily acids of the soap combine with the lime in the water, and the carbonic or sulphuric acid previously in com-

ination with the lime becomes united with the alkali of the soap. So long as any lime remains unprecipitated, the soap affords no lather with the water, but a very slight excess of soap suffices to form the lather.*

§ II. MATERIALS EMPLOYED IN SOAP-MAKING.

1. *The alkaline ingredient.*—The alkali employed in the preparation of soap should always be introduced into the “copper”† in a state of perfect causticity; no salt of the alkali, not even the carbonate, being well adapted to produce the saponification of oil. The solution of the alkali is always prepared by mixing the alkaline carbonate with lime and water, when the lime withdraws the carbonic acid of the alkaline carbonate to form insoluble carbonate of lime (chalk), the alkali being left in a caustic state in solution in the water.

The alkaline ley employed in the preparation of common yellow soap is made from “black ash” or “ball soda,” which is the residue of the calcination, in a reverberatory furnace, of a mixture of sulphate of soda, chalk or broken limestone, and small coal. When lixiviated with cold or lukewarm water, it affords a solution of carbonate of soda containing a

* The relative quantities of a clear solution of soap of known strength necessary to produce a lather on agitation with different hard waters would therefore afford an indication of the relative hardness of such waters. For the details of a process of this nature, contrived by Dr. Clark, see “Elements of Chemical Analysis,” page 249.

† The “copper” of the soap-boiler is the large iron boiler in which the saponification is effected.

small quantity of caustic soda and sulphuret of sodium.

The alkaline carbonate from which the ley intended for the preparation of white and mottled soap is made, is "soda-ash," which is obtained by lixiviating black ash in water, draining the solution from the insoluble matters, and evaporating to dryness. The residue thus obtained may be used for making ley; but as it generally contains some sulphur, the presence of which is an inconvenience in the process of soap-making, it is necessary for some purposes to calcine this residue at a moderate heat by means of a charcoal fire, whereby the whole of the alkaline sulphuret becomes decomposed and converted into carbonate. By lixiviating the mass in water, and evaporating the liquid to dryness, a residue is obtained of carbonate of soda nearly pure. When dry, it contains about 58 per cent. of pure soda.

The alkaline ley used in the preparation of soft soap is made from common potashes, which are prepared by calcining, in an iron pot, the residue of the evaporation of a ley obtained by digesting wood ashes in water. When of good quality, potashes contain 58 or 60 per cent. of pure potash.

In preparing the leys, the lime and alkaline carbonate are not mixed at once with the whole quantity of water required, but the water is made to percolate slowly through the mixture of lime and alkaline carbonate contained in round iron vessels, usually about five or six feet in diameter, and four or five feet in depth, furnished with a plug near the bottom. A filter of ashes supported on bricks is placed immediately inside the plug, and the vessel is nearly filled

with successive layers of quick-lime and black ash or white ash, the first layer being lime. Two parts of black ash require about one part of quick-lime : white ash requires a larger proportion. In all extensive soaperies from two to four such ley-vats are arranged together as one set at different elevations : the mixture of lime and alkaline carbonate in the first is that last made ; that in the second is in a fresher state than that in the third ; while that in the fourth is almost exhausted. Warm water is first allowed to percolate slowly through the weakest, and afterwards through the stronger in succession. The ley is employed at very different strengths for different purposes ; its density varying from 1·04 to 1·18. It always contains a considerable quantity of undecomposed carbonate.

The residuary mixture of lime and carbonate of lime, which is impregnated with a minute quantity of alkali, is made available in the glass manufacture, and also as a manure on stiff lands. A considerable quantity, intended for the latter purpose, has been sent from this country to the West Indies since the abolition of slavery.

2. *The unctuous ingredient.*—The following are the only oleaginous materials employed in the general way by the soap-makers of this country :

Tallow.	Whale oil.
Palm oil.	Seal oil.
Olive oil.	Cod oil.
Oil of grains (linseed and rapeseed).	Hog's lard.
	Kitchen and bone fat.

It has already been observed, that fixed oils and

fats contain, as they are met with in nature, two or more distinct compounds, possessed of a saline constitution, being composed of an organic base, called glycerine, in combination with peculiar unctuous acids. By far the greater number of fixed oils and fats that have been hitherto examined contain only three such compounds, stearine, margarine, and oleine; the leading properties of which, with those of their acids, may be here briefly adverted to.

Stearine,* or *stearate of glycerine*, which is the chief ingredient in tallow and suet, and the most important of the fatty bodies, may be prepared by melting mutton suet at a moderate heat, mixing it with about ten parts of ether and setting aside the mixture to cool. The soft, pearly scales which are deposited on cooling, after being subjected to pressure and washed with cold ether, are pure stearine.

Stearine is quite insoluble in water, but soluble in hot alcohol and ether; from both of which, however, it is almost entirely deposited on cooling. It fuses at about 140° or 145° Fahr., and congeals to a pulverizable mass devoid of any appearance of crystallization. It cannot be distilled in the air without decomposition.

Stearic acid may be prepared in a state of purity from the so-called "stearine" of commerce, used as a substitute for wax in making candles. This substance contains no stearine, but is the acid in question, contaminated with a little oleic acid, from which it may be completely purified by repeated crystallization from hot alcohol, until its point of fusion reaches 167° , which is that of pure stearic acid; though, when

* So named from *stear*, tallow.

once melted, it may remain liquid below 160°. This acid is insoluble in water, but soluble in alcohol and ether. In the fluid state it changes the colour of blue litmus paper to red, like other acids. The solid acid has a crystalline texture and is pulverizable. When heated *in vacuo*, stearic acid distils over with very little or without any alteration; but if air has access, it is converted into margaric acid, and another substance called margarone. Margaric acid is also the first product of the action of nitric acid on stearic acid.

The "stearine" of commerce is prepared by, 1°, saponifying tallow or lard; 2°, decomposing the resulting soap by an acid; and 3°, subjecting the mixture of stearic and oleic acids thus obtained to pressure between warm metallic plates, whereby the greater part of the oleic acid becomes expressed, while the stearic acid remains as a hard white mass possessed of a crystalline texture. On the Continent, the tallow or lard is boiled with an alkali to form soap, to which a solution of chloride of calcium (muriate of lime) is added. An insoluble mixture of stearate and oleate of lime is thereupon precipitated, which affords the mixture of the oily acids by being warmed with dilute sulphuric acid. In this country, however, where candle manufacturers (not being soap-makers also), are prohibited by law from having alkaline leys in their possession, the saponification is effected by lime alone. The disposition of the liquid acid to crystallize on cooling was formerly counteracted by the addition of about one thousandth part of arsenious acid. This deleterious substance is not, however, introduced at present. Stearine candles,

when properly made, are white and inodorous, and burn with as white a flame as wax. Their combustion, however, is a little more rapid than that of wax.

The composition of anhydrous stearic acid, according to Redtenbacher, is represented by the formula $C_{66} H_{66} O_2$; one equivalent of the acid, according to this formula, requires two equivalents of a base for its complete saturation.

Neutral stearate of potash ($2KO + C_{66} H_{66} O_2$) is a firm soap when cold, soluble in twenty-five parts of hot water, but more soluble in an alkaline solution. When a solution of this compound is mixed with a considerable quantity (one thousand parts to one of the stearate) of cold water, it is resolved into an acid stearate or bistearate of potash, which is precipitated, and free potash, which remains dissolved. When a solution of chloride of potassium is added to a concentrated alkaline solution of the neutral stearate, the latter is precipitated as a viscid mass, which becomes firm on cooling. If common salt is substituted for chloride of potassium, the precipitate consists of the neutral stearate of soda, which is harder and less soluble in water than the corresponding potash compound. Like the latter, it is decomposed when mixed with a great quantity of water (two thousand parts) into a bistearate, which precipitates, and free soda, which remains dissolved.

Margarine,* or *margarate of glycerine*, is solid at common temperatures, but more fusible than stearine. It is the principal constituent of human fat and goose fat, and is contained in most fats and oils. The

* So named from *μαργαρίτης*, a pearl, on account of the pearly lustre of margaric acid.

crystals which are deposited from olive oil on exposure to cold are a chemical compound of margarine and oleine (Liebig).

Margaric acid (the oily acid peculiar to margarine) is most easily obtained by heating impure stearic acid (such as the stearine used for making candles) with its own weight of common nitric acid for a few minutes. The fatty acid which is deposited as the solution cools contains a little oleic acid; to remove which, the mass is compressed between folds of blotting paper, and dissolved and crystallized from alcohol several times successively, till its melting point remains constant at 140° (Liebig). In appearance, margaric acid greatly resembles stearic, but it is more fusible. Its alcoholic solution has an acid reaction. The formula of the anhydrous acid is $C_{58}H_{96}O_6$.

Margaric acid, like stearic, forms with potash and soda neutral and acid salts, the latter containing half as much alkali as the former. The neutral salts are readily soluble in water, and the solutions afford precipitates of the acid salts or bimargarates when very largely diluted. The neutral margarate of potash is rather soft, but the neutral margarate of soda is somewhat harder. The formula of the neutral stearate of soda is $2NaO + C_{58}H_{96}O_6$.

Oleine, or oleate of glycerine, forms the principal constituent of oils, and may be obtained, though not in a state of purity, by subjecting congealed almond oil to pressure. The fluid portion which exudes is oleine, generally containing in solution either stearine or margarine, or both. At a very low temperature, oleine solidifies. If quite free from foreign matters capable of exciting a fermentative decomposition,

oleine does not become rancid, but this body is more liable to decomposition than either stearine or margarine. The oleine of drying oils appears to be a distinct substance from the oleine of fat oils (Redtenbacher).

Oleic acid is an oily liquid of a faint yellowish tint, having an acid reaction on test-paper, a very weak odour, and a pungent taste. When cooled to some degrees below the freezing point of water, it becomes a mass of crystalline needles. It is soluble in alcohol and ether, and is more easily decomposed than any other of the oily acids. The soapy compounds which oleic acid forms with potash and soda are both soft and very soluble in water, unless they contain an excess of acid. The composition of oleic acid has not been decided with certainty. According to the analysis of M. Varrentrapp, the formula of the hydrated acid is $\text{HO} + \text{C}_{18} \text{H}_{33} \text{O}_2$.

Glycerine.—In a state of purity, glycerine is a syrupy liquid, inflammable, inodorous, but very sweet to the taste, and was hence named by Scheele, its discoverer, the *sweet principle of oils*. It is miscible with water and alcohol in all proportions. It cannot be distilled alone without decomposition, but partially volatilizes when boiled with water. It is not fermentable, nor is it subject to spontaneous decomposition. In its solvent power on alkaline and metallic salts and other bodies, glycerine is nearly equal to water. It unites with sulphuric acid to form an unstable compound, which possesses the properties of an acid.

The most convenient method of preparing glycerine is to saponify olive oil with oxide of lead (litharge) and a little water, by boiling them together;

the soap of oxide of lead then formed is insoluble in water, but the liberated glycerine dissolves, accompanied by a small quantity of oxide of lead, which may be removed by passing a current of sulphuretted hydrogen gas through the liquid. After being filtered and carefully evaporated, the liquid leaves a residue of glycerine nearly pure.

It is obvious from what has already been stated, that the consistence of oils and fats must be related to the proportion in the oil or fat of oleine on the one hand, and of stearine and margarine on the other. If oleine predominates, it is liquid, and the temperature at which it solidifies is lower in proportion as the oleine is in excess; if margarine is the principal constituent, the consistence is about that of lard; but if stearine is most abundant, the fat is firm, like mutton suet. The principal oily and fatty matters hitherto minutely investigated, which contain in combination with glycerine other fat acids than those which have just been described, are, palm oil, train oil, butter of the cow, butter of nutmegs, butter of the cocoa-nut, the fat of the goat, and castor-oil.

Besides stearine, oleine, and margarine, most oils and fats contain in their ordinary state small quantities of foreign colouring and odoriferous matters, which vary with the different kinds, and which may be removed without affecting the essential characters of the oil or fat.* They also contain more or less albuminous or similar azotized matters common to all

* In most cases, such matters may be almost entirely removed by digesting the oil or liquefied fat with animal charcoal for twenty-four hours. The foreign bodies present in oils used for burning in lamps considerably decrease the brilliancy of the flame and also tend to clog

plants, as membrane and mucus, which act like yeast in exciting a fermentative decomposition of many organic bodies with which they are in contact. To the presence of these matters, the rancidity which most oils acquire on exposure to the air, partly through the absorption of oxygen, may be ascribed; for pure stearine, margarine, and oleine do not become rancid on exposure to the air. A rancid oil contains the oily acids in a free state, and a volatile body to which the peculiar odour is due.

Many oils, when exposed to the air, become converted through the absorption of oxygen into a tough, transparent, resinous mass or varnish, which does not afford an oily stain to paper; but others do not dry on exposure to the air, though they may become somewhat more consistent. Hence a well-marked distinction of oils into two classes, drying oils and fat oils. The former form soft soaps with alkalies, and the latter, if of vegetable origin, hard; and the former do not solidify like the latter when mixed with nitrous acid, or nitrate of suboxide of mercury. The oleic acid of drying oils appears to be a distinct sub-

the wick. Oil intended for burning may be conveniently purified by strongly agitating it with two or three parts per cent. of concentrated sulphuric acid, which would have no action on the oil, but cause the separation of the foreign matters in brown flocks. The mixture should be allowed to remain at rest for twenty-four hours, and be then heated by introducing steam, till its temperature rises to 160° or 170° Fahr. It is then allowed to stand quiet for three or four days, during which time it settles into three strata: the uppermost stratum is the purified oil, which should be washed with water, and filtered through cotton placed between perforated metallic plates; the middle stratum is brown impure oil, from which, after a time, an additional quantity of pure oil may be obtained; and the lowermost is water charged with sulphuric acid and the products of the decomposition of the foreign matters. Such a process as this was long ago devised by M. Thénard.

stance from the oleic acid of fat oils. It dries in the air to a resinous mass, like the oil from which it is derived.

Tallow is the concrete fat of oxen, deer, and large quadrupeds in general, melted and separated from the fibrous matter with which it is at first accompanied. It consists chiefly of stearine, with a little oleine, and is firm, brittle, and has a peculiar and heavy odour. It soon becomes rancid on exposure to the air. As met with in commerce, it usually has a yellow tinge; but when pure it is white, and nearly insipid. It is divided into two chief varieties, according to its purity and consistence, namely, candle and soap tallow; and these are subdivided into other classes, according to the colour of the tallow, and (if foreign) to the place from whence it is imported. Its quality depends in some degree on the animal from which it is procured; but more, probably, on the care observed in its preparation. It is generally sufficiently pure to be used in soap-making without any previous purification.

Besides a great quantity of tallow supplied by the home slaughter, about sixty thousand tons per annum are regularly imported into the United Kingdom, by far the greater part of which is brought from Russia. Of late years, considerable importations of tallow have been made from the States of the Rio de la Plata. The price of "soap tallow" from St. Petersburg and Siberia is generally about two pounds or guineas per hundred-weight, and that of British a little higher.

In the manufacture of the coarser kinds of white

soap, a considerable quantity of the heterogeneous substance known by the name of "kitchen stuff" is consumed, after being refined by melting, washing, and straining. The price of this article in the rough state is generally about twenty-five shillings per hundred-weight.

Palm oil.—This important article of commerce is derived from the fruit of the *Elais Guianensis*, or oil-palm (considered to be identical with the *avouira elais* of Aublet), which grows on the west coast of Africa, to the south of Fernando Po. This tree also grows in Brazil; but the commercial demand for the oil is exclusively supplied from the west of Africa, where the palm is made an object of extensive cultivation. The fruit of this tree is of a golden-yellow colour on the outside, and about the size and shape of a pigeon's egg. To obtain the oil, the fleshy covering of the fruit is said to be detached from the kernel, and bruised into a paste, which is agitated with a quantity of boiling water. On standing, the oil rises to the surface, and concretes, as it becomes cold, into a mass of the consistence of butter.

When fresh, palm oil is of an orange-yellow colour, has a sweetish taste, and the odour of violets; its fusing point is then 81° Fahr., but old palm oil does not melt at a lower heat than 90° or 96°. By exposure to the air palm oil soon becomes rancid, both glycerine and the fatty acids being liberated. This oil contains about two-thirds of its weight of a peculiar white solid fat, to which the name of

*palmitin** has been given. The remainder is principally oleine.

Few articles have increased so rapidly in commercial importance, of late years, as palm oil. Though introduced as an article of commerce within the last forty years, it is now regularly imported into this country to the amount of near twenty thousand tons annually; and nearly the whole of this quantity is consumed in the soap manufacture. A trifling quantity is also used in perfumery. Mr. Jamieson has shewn, in his pamphlet on the importance of our trade with the West Coast of Africa, that the trade in palm oil has been the principal instrument in the reduction of that in slaves. The oil is procured by barter of goods of British manufacture, and the trade is free from those fiscal regulations which impede our commerce with old states. The present duty on this article is sixpence per hundred-weight. To the British soap manufacturer it is cheaper than tallow to the amount of about ten pounds per ton.

To melt the oil for the purpose of withdrawing it

* *Palmitin* is analogous in its chemical constitution to *stearine*, &c., being a compound of oxide of glycerule with a fatty acid, which has been called *palmitic acid*. *Palmitin* may be obtained pure by subjecting palm oil to pressure, washing the residue with hot alcohol, dissolving it in hot ether, in which it is very soluble, and crystallizing. It fuses at 118° ; and congeals, on cooling, into a friable mass, similar to wax. *Palmitic acid* is obtained by saponifying palm oil with a caustic alkali, and decomposing the resulting soap by a strong acid. A little oleic acid accompanies the *palmitic acid* thus prepared, but the former may be separated by solution in alcohol and by pressure. *Palmitic acid* resembles *margaric acid* in appearance; its fusing point is 140° . According to Dr. Stenhouse, the formula of *palmitic acid*, in its hydrated state, is $\text{HO} + \text{C}_{31}\text{H}_{51}\text{O}_2$, and that of *palmitin* $\text{C}_{33}\text{H}_{53}\text{O}_4$, or $\text{C}_3\text{H}_5\text{O} + \text{C}_{30}\text{H}_{41}\text{O}_3$. *Glycerine* is represented by $\text{C}_3\text{H}_5\text{O}$.

from the casks in which it is imported, it is common to introduce steam within the cask by a pipe, the cask being placed over a trough with its bung downwards. By the time it reaches this country, palm oil is generally of a deep orange-red colour, and hence cannot be employed in making soap without undergoing a process of bleaching. The bleaching is carried to a greater extent when the oil is intended for the preparation of white than of yellow soap. The substance which is the source of colour is not proper to the pure oil, the constituents of which, when in a state of chemical purity, are colourless; it is a product of the spontaneous decomposition of a peculiar principle derived from the palm, and is capable of being decomposed and decolorized at a high temperature by all the ordinary bleaching agents, as chlorine, chromic acid, the air, &c.

The most ready, but most expensive, mode of bleaching palm oil is probably that patented a few years ago by Mr. Watt, the bleaching agent in which is chromic acid, or rather nascent oxygen, produced through the decomposition of chromic acid. In this process the oil is first of all heated in a common steam boiler for half an hour, then allowed to settle, and when cooled down to 130° Fahr. is decanted from the sediment and the water formed by the condensation of the steam, and placed in wooden vessels, each capable of containing about half a ton. To each ton of oil thus far freed from extraneous matters is added the following mixture: twenty-five pounds of bichromate of potash dissolved in water so as to make a saturated solution, eight pounds

of concentrated sulphuric acid, and about fifty pounds of strong muriatic acid; or instead of the muriatic acid, the same weight of common salt may be introduced, together with a sufficient quantity of sulphuric acid for its decomposition.* After being well agitated with this mixture for a few minutes, the oil changes in colour, becoming first black, then dark green, and soon afterwards light green, when a thick froth appears on the surface. The appearance of a light green colour and a froth is an indication of the completion of the process. If a little of the oil, when taken out and allowed to settle, does not appear sufficiently decolorized, an additional quantity of the bleaching mixture may be added. It is stated that a ton of oil may be rendered quite colourless by this process in five minutes.

The oil is next allowed to remain undisturbed for about half an hour, for the aqueous solution of chloride of chromium, sulphate of potash, and other foreign matters to subside; after which it is pumped off from this sediment into a wooden vat, mixed with a little fresh water, and heated for a short time by the introduction of steam. After being once more allowed to settle, it may be decanted fit for use.

In this process, the oxidation of the colouring matters of the oil is effected by chromic acid, liberated from the bichromate of potash by the sulphuric or rather muriatic acid. The chromic acid yields oxygen to the colouring matters, and becomes reduced to the state of green oxide of chromium, which, by the

* Such are the materials and their proportions recommended by Mr. Watt. Most bleachers of palm oil, however, take twenty pounds of bichromate of potash and about forty pounds of commercial muriatic acid.

action of muriatic acid, gives rise to chloride of chromium.* The latter is found, when the mixture with the oil has settled, dissolved in water at the bottom of the vat, and may be made available in the preparation of more bichromate of potash or chromate of lime.

This process was very extensively followed in the soap manufactories of this country a few years since; but being expensive, it is not generally practised at present, except in purifying oil intended for preparing white soap. The expense of decolorizing a ton of oil in this way is generally about thirty shillings.

Chlorine is not so well adapted for bleaching palm oil as chromic acid. The colouring matter of the oil is readily decomposed by chlorine; but the latter exerts an injurious action on the oil itself, causing it to become of a brown colour, and injuring its consistence. This bleaching agent has been used, however, for decolorizing palm oil on the large scale; the materials for generating the chlorine, namely, black oxide of manganese, sulphuric acid, and muriatic acid, being introduced directly into the melted oil. Considerable inconvenience was formerly experienced in this process from the slowness with which the minutely divided oxide of manganese subsided from the oil, but this is now completely surmounted by enclosing the manganese in a cloth bag.

In a method of bleaching palm oil introduced into the soap manufactories of Liverpool about six years since, the discharge of the colouring matter was

* The hydrogen of the muriatic or hydrochloric acid unites with the oxygen of the oxide of chromium to form water, while the chlorine and chromium unite at the same time to form a soluble compound.

affected by exposing the oil, contained in a strong cast-iron boiler built over a furnace, to the temperature of 450° , which completely decomposes the colouring matter without being injurious to the oil. By the time the oil near the surface became heated to 450° , that near the bottom of the boiler frequently acquired a temperature higher than 600° , when it became carbonized and partially converted into gas. A considerable portion of the oil hence frequently acquired a black colour from intermixture with the carbonized oil at bottom, and another inconvenience in this plan consisted in the explosions which sometimes resulted from the disengagement of inflammable gas. For these and some other reasons this method has been very generally abandoned.

If freely exposed to the air, the palm oil may be completely decolorized at a temperature far below 430° , and even below 212° . The process requires a considerably longer time, however, with these comparatively low temperatures.

Mr. Cameron's process for bleaching palm oil is conducted in the following manner.* The oil is introduced into a cast-iron pot, capable of holding from three to four tons of oil, fixed over a small furnace, and furnished with two or more pipes for the circulation of steam, and a horizontal revolving fan of sheet-iron for the purpose of agitating the oil. By means of a fire in the furnace underneath, the oil is heated to the temperature of 230° ; the fire is then withdrawn, but the temperature of the oil is maintained at that point by introducing high-pressure steam from a boiler loaded with fifteen pounds on

* Transactions of the Society of Arts.

one square inch of the valve, until the oil is sufficiently deprived of its colour. During the whole process the oil requires to be agitated for the purpose of bringing it into more complete contact with the air, the oxygen of which is the principal agent concerned in the decoloration. The agitating fan may be revolved at the speed of about six revolutions per minute. It is stated that four tons of oil may be bleached in this manner in ten hours, at one operation, at an expense of from eight to twelve hundred-weight of small coal.

All that is essential in this mode of bleaching is obviously the exposure of the oil to the combined influence of air and heat, many modes of accomplishing which might be devised. In a process for bleaching oils and fatty matters, of this nature, made the subject of a patent by Mr. Arthur Dunn in 1843, the air is forced below the surface of the oil through pipes by means of a blowing apparatus, and then allowed to rise through the liquid in numerous small streams; the oil being maintained at a temperature between 170° and 230° Fahr. by steam-pipes or other means. A hood communicating with a chimney is placed over the vessel containing the oil, for the purpose of conducting away the unpleasant vapours which are disengaged.

The oxidizing action of the air on the impurities in palm oil seems to be accelerated by combining the influence of light with that of heat. With the view of accomplishing this, the oil is sometimes placed in a thin stratum in a large, shallow, uncovered vat, similar to the coolers used in brewing for the purpose of rapidly reducing the temperature of the wort pre-

vious to fermentation. Several such vats, each about one foot in depth, may be heated by means of steam passed through serpentine leaden pipes proceeding from a common boiler: one extremity of each tube may terminate in a receiver for the condensed water which may be returned to the boiler. Each vat is first two-thirds filled with water; when this is become hot, a sufficient quantity of palm oil is introduced, to form, when fluid, a stratum of about two inches in depth, which should be maintained during the whole process at a temperature as near 212° as possible. To preserve an equal temperature at different parts of the vat, the steam may be admitted at opposite ends, and circulated in opposite directions, by two distinct serpentine tubes. Both air and light having access, the time required for the decoloration of the oil at a temperature near 212° is from ten to fifteen hours; the thinner the stratum of oil, the more rapid is the process. M. Payen has ascertained, in operating on the small scale, that the rapidity of the bleaching action is not sensibly lessened by loosely covering the containing vessel with a plate of glass, provided the renewal of the air over the surface of the oil is not much interfered with;* and hence suggests to manufacturers the propriety of adopting such an expedient on the large scale, for partially preventing the great loss of heat which occurs from the extensive surface of oil presented to the air in the open vessels commonly used in this mode of bleaching the oil. While fluid, the blanched oil

* If exposed to the temperature of 212° in a closed glass vessel, so that light and heat have access, but not air, the oil does not become blanched.

retains a fawn-coloured tint; but when cold and solid it is greyish-white.

Strong nitric acid (the nitrous acid of the shops) has been successfully applied to palm oil as a bleaching agent. To procure oil perfectly colourless, two gallons of acid of sp. gr. 80° Tw. (1.400) should be mixed with five tons of the oil to be decolorized. The oil may thereby be rendered perfectly colourless at a very moderate expense; but it is apt to become slightly coloured by keeping, and the soap made with the oil thus bleached is also coloured.

Of all these methods of bleaching palm oil, that which effects the decomposition of the colouring matter most completely is Mr. Watt's process by means of bichromate of potash, but the expense of this mode precludes its extensive adoption except for oil used in making the finer kinds of soap. When once perfectly blanched by this process, the oil may be preserved without acquiring colour, and the soap made from it does not become coloured, like that made from oil bleached by the air and heat, or by means of nitric acid. When the oil is to be used for making yellow, and not white soap, the most convenient mode of bleaching, having regard to economy, is by the action of the air, the oil being *moderately* heated. It seems that the colour does not reappear to so great an extent when the oil has been moderately heated (say, to 180°), as when it has been maintained at a temperature above 212°; it should be heated to 212°, however, at the commencement of the process, and then be allowed to cool a little. The oil does not become sensibly bleached when only moderately heated so long as water is present; but when all moisture

is dissipated, the blanching commences immediately.

When rancid palm oil, which always contains free acids, is mixed with a ley containing sulphuret of sodium, a considerable quantity of sulphuretted hydrogen gas is disengaged, through the decomposition of the alkaline sulphuret by the acid. In mixing the materials for yellow soap, sufficient sulphuretted hydrogen is sometimes emitted to completely stupefy the workmen.

Rosin.—This substance forms an important ingredient in the composition of yellow soap. It is procured by the distillation of the yellowish-grey, semi-fluid body, known by the name of *turpentine*, which is an exudation from incisions made in the stems of various species of the pine-tree. Several varieties of turpentine are met with in commerce, having distinctive names, according to the countries from whence they are procured, and the trees from which they were extracted. When distilled along with water, all these turpentine (or *balsams*, as some of them are termed) afford a volatile oil or essence, and leave a solid resinous residue, which in the case of common turpentine, extracted principally from the *Pinus abies* and *Pinus sylvestris*, is rosin or colophony. The distilled essence is oil of turpentine.

Though employed in the manufacture of soap in the place of a fixed oil or fat, rosin is not to be considered analogous to a fat in its chemical constitution, or to be capable of forming with an alkali a proper soap by itself. Rosin contains no glycerine, nor any equivalent for that substance, but is an in-

definite mixture of three distinct bodies possessing well-marked acid properties, each of which is capable of combining with alkalies, and readily dissolving in alkaline solutions, though quite insoluble in water. The compounds of these resinous acids with soda cannot be separated from their solutions in water by common salt, like true soda soaps, nor do their concentrated solutions become mucilaginous or gelatinous on cooling. Such solutions, however, produce a lather when agitated, like a solution of soap.

The three resinous acids which constitute common rosin have been named *sylvic*, *pinic*, and *colopholic*. *Sylvic* acid may be dissolved out of rosin by weak alcohol, in which *pinic* acid is insoluble. The latter may be dissolved by strong alcohol. *Colopholic* acid is a product of the action of heat upon *pinic* acid, formed during the distillation of the oil of turpentine. It is brown, and the chief cause of the colour of common rosin; *pinic* and *sylvic* acids being colourless when pure. It is volatile, and may be procured by distilling *pinic* acid.

§ III. MANUFACTURE OF HARD SOAP.

The boilers or "coppers" employed in this country in the soap manufacture are made of cast-iron in three principal pieces, commonly joined together by a cement made with iron-rust,* *sal-ammoniac*, and sul-

* Lead is sometimes used as a solder to join the pieces of the soap-pan, instead of iron-rust cement; the former being preferred in consequence of the facility with which it may be removed when the pan becomes cracked; but in other respects it is decidedly inferior to iron-rust cement.

phur; the top and middle pieces, called "curbs," are firmly set in masonry; the fire has direct access only to the lowest piece or "pan," which may be easily removed should it become cracked, without disturbing the masonry. The usual source of heat is a small open fire-place; but in some soaperies, heat is applied by introducing steam.

White Soap.—The unctuous material commonly employed in this country and the north of Europe generally in the preparation of white soap is tallow; a small proportion of white soap is also made from well-refined palm oil. In France, almost the only unctuous matter employed in making this kind of soap is olive oil, of inferior quality. The proper alkali is soda, whether oil or tallow be used. The whole quantity of tallow or oil consumed in making one batch of soap is commonly introduced into the soap-pan at one time, but the alkali is applied several times successively. To produce one ton of soap, there are required from ten to fourteen hundred-weight of tallow, or about the same quantity of olive oil.

The average composition of ordinary white tallow soap may be taken at, alkali one part, and fatty acids about nine parts; with from five to eight parts of water. In different kinds of soap, the proportion of tallow or oil ranges between seven and eleven parts to one of alkali, and the proportion of water between thirteen and fifty parts to one hundred of perfectly dry soap. Allowing one part of pure alkali for nine parts of tallow, and supposing the leys to be completely deprived by the tallow of their caustic alkali,

a ton of tallow would require 4.6 hundred-weights of soda-ash containing 48 per cent. of pure soda. A much larger quantity of alkali, however, is found to be necessary in practice, as the leys are seldom perfectly caustic, and never wholly deprived of their alkali. In making Windsor soap, of the best quality, the tallow is generally mixed with about ten per cent. of inferior olive oil.

The entire quantity of tallow,* mixture of tallow and lard or olive oil, or palm oil, to be used at one operation, which we may suppose a ton, having been introduced into the boiler, from one hundred and fifty to two hundred gallons of soda ley of specific gravity 18° Tw. (1.090) are added, and the mixture is gently boiled. After ebullition for one or two hours, the whole forms a viscid emulsion, capable of being drawn out into clear threads. In this state, the soap which has been formed is dissolved in the ley, and must be separated before the spent ley can be withdrawn and a fresh one applied. A method of separating the soap now commonly resorted to both in this country and on the Continent, consists in the application of common salt, which dissolves in the liquid, and causes the soap, which is perfectly insoluble in a strong solution of salt, to rise to the surface. When salt is not added for this purpose, the separation of the soap is effected by the saline matters present as impurities in the ley. The separation

* By far the greater quantity of white soap made in this country is made from tallow and soda only. As this soap is inconveniently hard, some manufacturers make a softer and finer article by substituting for one-fourth part of the tallow as much lard, of which considerable quantities are now imported from North America.

is known to be complete by placing a little of the mixture on a flat surface, when the fluid ley flows off and leaves the soapy paste behind. When the soap is completely separated, the liquid ceases to froth on ebullition.*

* The following observations, by Professor Liebig, describe more fully the comportment of soap with a solution of common salt (*Annalen der Chemie und Pharmacie*, xxxvii).

"If a piece of common hard soap is put into a saturated solution of salt, at ordinary temperatures, it swims upon the surface without being moistened, and if heated to ebullition, it separates without foam into gelatinous flocculi, which collect on the surface, and on cooling, unite into a solid mass, from which the liquid flows off like water from fat. If the flocculi are taken out of the hot fluid, they congeal, upon cooling, into an opaque mass, which may be pressed between the fingers into fine laminæ without adhering to them. If the solution is not quite saturated, the soap then takes up a certain quantity of water, and the flocculi separate through the fluid in boiling. But even when the water contains $\frac{1}{100}$ th of common salt, ebullition effects no solution.

"If the soap is boiled in a dilute and alkaline solution of salt, and suffered to cool, it collects on the fluid in a more or less solid state, depending on the greater or less concentration of the solution, that is, on the quantity of water taken up by the soap. By boiling the soap for a considerable time with a dilute solution of salt, the watery flocculi swell up, and the mixture assumes a foaming appearance; but still they are not dissolved, for the solution separates from them. The flocculi, however, have become soft and pasty, and even remain so when cold, and their pastiness depends on the quantity of water they have imbibed. By continuing the ebullition, this character again changes, and in proportion as the evaporation of the water renders the solution more concentrated, the latter again extracts the water from the flocculi; the liquid, however, continues to froth, but the bubbles are larger. At length the point is attained at which the solution becomes saturated; the large iridescent bubbles formed just before this, disappear, and the liquid continues to boil without froth; all the soap collects as a translucent mass on the surface, and the solution and soap cease to attract water from each other. If the plastic soap is now removed, and cooled, while the solution is pressed out, it becomes so solid as scarcely to receive an impression from the fingers. In this state it is called *gruin-soap* (*Kernseife*).

"The addition of salt, or its solution, to a concentrated alkaline solution of soap in water, precipitates the soap in gelatinous flocculi, and the mixture comport itself precisely like solid soap boiled with a dilute solu-

The fire having been withdrawn, and the contents of the soap-pan allowed to become cool, the spent ley is pumped off, and about the same quantity as before of fresh ley, of a density near 28° Tw. (1.140) is in-

tion of salt. Carbonate of potash and caustic potash act precisely like salt, in separating soap from the alkaline fluid.

"The application of the above to the manufacture of soap is obvious. The fat is kept boiling in an alkaline ley until all pasty matter disappears, but the ley should have only a certain strength, so that the soap may be perfectly dissolved in it. Tallow may be boiled for days in a solution of caustic potash of specific gravity 1.25 without saponification; with a stronger ley, a partial saponification takes place, but being insoluble in the fluid, the soap floats on the surface as a solid mass: by the gradual addition of water and continued boiling, the mass, at a certain point, suddenly becomes thick and clammy, and with more water a kind of emulsion is formed, which becomes perfectly clear and transparent on continued heating, if a sufficient quantity of water is present. In this state, it may be drawn out into long threads, which, when cold, either remain transparent, or are milky and gelatinous. As long as the hot mass, suffered to drop from a spatula, exhibits a milkiness or opalescence, the boiling is continued, or more alkali is added. When excess of alkali is present, the milkiness arises from imperfect saponification, or want of water; the former is shewn by dissolving a little in pure water, which becomes perfectly clear if the whole is saponified. If the ley contain lime, the mixture is also turbid, but the addition of an alkaline carbonate instantly causes the turbidity from that source to disappear. In order to separate the soap from water, free alkali, and glycerine, a large quantity of salt should be gradually added to the boiling mass, one portion being entirely dissolved before the next is added: the first addition increases the consistency of the mass, while each successive portion renders it more fluid, till it loses its adhesive character, and drops from the spatula in short thick lumps."

In being separated by means of salt from a very dilute solution, soap suffers an alteration in composition, the separated soap being a bistearate, binoleate, and bimargarate of the alkali, instead of the neutral compound originally in solution; but when the solution of soap is of moderate strength, the soap is separated without alteration in composition.

Cocoa-nut oil, which has been used to a small extent in the manufacture of white soap, affords a soap which requires for its separation from alkaline leys a much larger quantity of saline matters than the soaps of tallow, palm oil, and olive oil. Cocoa-nut oil is moreover very difficult to saponify, at least on the large scale.

troduced. The mixture is then boiled for a few hours, until nearly the whole of the free alkali has been taken up, and the soap again separated from the liquor, when the fire is again withdrawn, the mixture cooled, and the spent ley pumped off. These operations are several times repeated with leys gradually increasing in strength to 36° Tw. (1.180), until the soap tastes slightly alkaline, feels dry and not oily to the fingers, and presents certain appearances indicative of a sufficient action of the alkali; in general, two or three boils are given daily for as many days.* The boiling with ley several times successively serves not only to complete the saponification, but to wash and purify the soap.

In Germany, where potash is just as accessible as soda, hard soap is made by a process very different from that followed in this country. The oil or tallow is first completely saponified by means of potash ley, and the potash soap thus formed is decomposed by adding a considerable quantity of common salt, which gives rise to the formation by a double decomposition of a soap of soda and chloride of potassium. The change is simply a transposition of the potassium in the soap and the sodium in the common salt. As chloride of potassium does not cause the separation of soda soap from its aqueous solution like common salt, it is necessary to apply considerably more of the latter than is necessary for the mere decomposition. The above process was formerly pursued in this country, but the high price of potash, and the low price

* When kelp was used in the soap manufacture instead of soda-ash, and weaker leys employed than at present, three boils were frequently given for six successive days.

and good quality of British soda-ash, have led to its entire rejection.

When the soap is properly formed, and completely separated from the ley, it is removed from the soap-pan, being in a pasty state, conveyed in buckets to the "frame-room," and poured into the rectangular cisterns called the "frames," or "sesses," in the soap-eries of Liverpool, to solidify. The frames in common use for white and mottled soap, and also for yellow soap until recently, are made of wood, and consist of a pile of equal rectangular frames measuring internally forty-five inches by fifteen inches, the thickness or height of each being about four inches. These frames being made very smooth, so as to fit closely together, are piled one upon another to the height of from five to twelve feet, thus forming a square well often large enough to contain more than two tons of soap. The frames are bound tightly together by means of iron screw-rods. For cooling and solidifying yellow soap, frame-moulds made of cast-iron have of late been introduced, such frames being composed of five rectangular plates (one for the bottom, two for the ends, and two for the sides), so arranged and fastened together as to form a well of the same length and breadth as the wooden frames, and about five feet in height. These frames are put together and taken abroad with more facility than the wooden frames, and the good conducting power of the iron considerably accelerates the cooling of the soap. The internal length and breadth of the frame are regulated by the Excise, but the depth is left to the convenience of the manufacturer, excepting that it must not be less than forty-five inches.

As soon as the soap is put into the frames, it is mixed with a small quantity of water, and well agitated with a wooden pole called the "crutch" until nearly cold. If allowed to solidify in the state in which it is withdrawn from the copper, the soap would have a rough granulated texture, and be very hard (if made from tallow and soda only); but it acquires a finer grain, and becomes softer, by being agitated with a little water.

When the mass of soap has solidified and become cold, the iron screw-rods which bind the frames together are removed, and each frame is lifted off the soap, which is left as a compact mass of the size of the interior of the frame. This mass is then cut by means of a wire into slabs of two or three inches in thickness, which are subdivided by a machine into the bars in which the soap is sold. The bars are piled away one upon another crossways, in the form of a wall, interstices being left for the circulation of air; in which state they are allowed to remain for a short time, to allow of the exudation of the saline solution with which the soap is still impregnated to a small extent.

As the exhausted leys, which are pumped out of the soap-copper, are not wholly deprived of their free alkali, and contain sulphate of soda besides, they should be evaporated to dryness and the residue be calcined with lime-stone and small coal, in order to obtain the alkali in the state of carbonate.

Mottled Soap.—Mottled or marbled soap is made from the same kind of materials as white soap, but the tallow for the former is selected with less care

than that for the latter, and the heterogeneous fatty substance known as "kitchen-stuff" generally forms one of the materials for mottled soap. The process of saponification is conducted in just the same manner for mottled as for white soap, the principal difference consisting merely in the relative time allowed for the separation of the soap from the last ley, before it is transferred to the frames; mottled soap being removed earlier than white soap. The brown veins in mottled soap are due to the presence of exceedingly minute traces of sulphuret of iron derived from the last service of ley, in which the sulphuret was dissolved, probably in combination with alkaline sulphuret, for leys containing sulphuret of sodium yield far more iron to the soap than those which contain none. While the soap is in the frames, the ley diffused through it unequally, slowly separates as the soap cools, and leaves in its track the brownish veins. A perfectly colourless ley, apparently free from every trace of iron, may, nevertheless, contain quite sufficient to produce mottling, if allowed to separate from the soap slowly. In some soaperies the mottling is produced by sprinkling on the surface of the soap, after being boiled with the last service of ley, a small quantity of very strong and sulphuretted ley, which produces the mottling by filtering slowly through the mass of soap.*

* That the colour of the veins of mottled soap is due to iron, seems evident from the fact that the ash which remains after the calcination of the brown parts of such soap affords to reagents a sensibly larger quantity of iron than the ash of the white parts of the same piece of soap. The iron is, no doubt, principally derived from the rust on the cisterns in which the leys are made. In France, the mottling is produced by adding

Silicated Soap.—The true silicated soap, made according to Mr. Sheridan's patent, consists of a mixture of silicate of soda with hard soap. The silicate of soda is prepared by boiling the powder of flints in a strong caustic ley, until the compound attains about twice the density of water. When of that strength, it contains, according to Dr. Ure, about thirty-five parts of silica, and forty-six of hydrate of soda, in one hundred parts. This compound is added to hard soap in a liquid or gelatinous state, and the mixture is well triturated in an iron pan, and then conveyed to the frames to solidify. The detergent properties of the soap thus made are very considerable. But the soap now sold under the above name is generally made by mixing with the pasty soap while in the frames a quantity of china clay, previously well rubbed up with a little caustic ley. As the clay possesses, of itself, no detergent property, its addition to the soap can only be regarded as an adulteration. The soap of English manufacture, which paid duty in 1842 as silicated soap, amounted to nine hundred and sixty tons. The whole of this quantity, however, might not have been silicated, for any kind of soap which possesses a greater density than 1.050 is considered by the Excise to be silicated, though it may not contain a particle of silica. This soap generally contains about one-fifth of its weight of silica or china clay.

Yellow Soap.—The essential difference between yellow soap and all other kinds is due to the pre-

to the soap, during the boiling, a very small quantity of solution of sulphate of iron (copperas).

scent in the former of a considerable quantity of resin, which, as before observed, is capable of uniting with alkalis to form a detergent compound soluble in water (page 319). The unctuous ingredient introduced into this soap, besides the resin, was formerly tallow, but of late years palm oil has been very largely used. The usual proportions of palm oil and resin are three and a-half parts of the former to one of the latter:* if made with a larger proportion of resin, the soap is soft and dark-coloured. Since the compound of resin and soda does not separate, like soap, from an alkaline solution on concentration, it would be improper to have the resin present in the copper while the palm oil is being brought through all the stages of the saponifying process, as a portion of the resin would, in that case, be removed with the spent leys. When the saponification of the palm oil is nearly complete, namely, at the last charge of ley, the resin should be introduced in a state of coarse powder, and well mixed with the soap by agitation. The mixture is then boiled for some hours, (a small quantity of ley being occasionally added, if necessary, to preserve an excess of alkali,) until the soap is fully formed, when the ley may be withdrawn, and one or two waters or else weak fresh leys applied successively with agitation, for the purpose of washing and purifying the soap. The resinous scum being removed for another operation, the soap may be conveyed to the iron frames (page 326) to solidify. Yellow soap usually contains to one part of alkali (soda) from

* The extreme proportions are, three parts of oil to one of resin, and nine parts of oil to two of resin.

ten to eleven parts of oil or fat and rosin, with from twenty-four to fifty per cent. of water. The yellow soap which contains a large proportion of water, has just the same appearance as that which contains only a small proportion. When the soap contains anything like fifty per cent. it has been added while the soap is in the frames for the purpose of sophistication.

Transparent Soap.—This fancy soap is made by gently heating, in a copper still, equal weights of white tallow soap cut in shreds and made perfectly dry, and spirits of wine, a little turmeric or archil being added as a colouring matter. When the spirit has taken up as much of the soap as it is capable of dissolving, the source of heat is withdrawn from the still, and the solution allowed to settle for a few hours, after which it is poured into tin frames to become solid. After exposure to dry air for a few weeks, the mass becomes transparent, and is then fashioned into the cakes in which it is sold.

§ IV. MANUFACTURE OF SOFT SOAP.

The manufacture of soft soap is much simpler than that of hard. This article differs considerably from hard soap in its consistence and general appearance, and is made from different materials, potash and either a drying oil or a fish oil being essential ingredients. It is more alkaline and more soluble in water than hard soap, and is principally used for cleansing stuffs of wool and silk.

The fish or drying oil, either alone or mixed with tal-

low or a vegetable fat oil, is boiled with weak potash ley until the saponification is complete, more ley being added occasionally if required; but no waste leys are pumped off, as in the manufacture of hard soap. Soft soap is insoluble in moderately strong potash ley, and may be precipitated from its solution in water by the addition of a strong ley; hence arises a necessity for employing ley of a certain state of dilution. If the ley is in too small proportion, a bin-oleate of potash is formed, which adheres to the bottom of the soap-pan in thick masses; by the addition of more ley it becomes the neutral oleate.

In this country, tallow is always introduced in small quantity as one of the materials for soft soap, being added for the purpose of producing the solid white granulations of stearate of potash called "fig-ging." Hence British soft soap presents the appearance of a brownish transparent body through which white grains are disseminated. On the Continent, this kind of soap is sometimes made without tallow or fish oils.

Oils require for their saponification a larger proportion of potash than of soda, one part of pure potash being capable of completely saponifying only from four and a half to five parts of oil. Potash soaps also always contain about half their weight of water, chiefly in a state of mechanical admixture, besides glycerine, carbonate of potash, caustic potash, and saline impurities introduced with the ley, which are not removed as in the manufacture of hard soap by pumping off the waste ley. By applying strong alkaline leys towards the completion of the process, the soap might be separated from the ley, and the saline

impurities and glycerine removed by pumping out the ley; but such a plan is never resorted to on the large scale. Since potash soaps contain so much water, &c., a given quantity of oil yields a considerably larger quantity of soap with potash than with soda. The general composition of soft soap may be taken at, alkali one part, fatty acids from four and a half to five parts, water and impurities from five to six parts.

In some soaperies the whole of the oil and tallow is introduced at once, together with a portion of the ley, and the remainder of the ley is added after some hours' gentle ebullition; but in others both the oil and ley are introduced gradually. When the mass is become transparent, ceases to have an acrid taste, and assumes the proper consistence on cooling, the saponification is considered to be complete, and the soap is transferred to the barrels or casks in which it is sent out of the soapery. The green tinge in Continental soft soap is communicated by adding a little indigo, which has been previously boiled with water, or brayed with weak potash ley. Some oils produce a greenish-coloured soap without indigo.

The figged granulations of stearate of potash do not usually make their appearance until two or three weeks after the soap has been made; in very warm weather they do not appear at all. They are improperly considered to be a proof of the good quality of the soap, and hence the figged appearance has been imitated by the addition of starch.

EXTRACTS FROM "STATEMENTS RELATING TO THE SOAP DUTIES; PREPARED BY DIRECTION OF A GENERAL MEETING OF SOAP MANUFACTURERS OF ENGLAND, HELD MARCH 13th, 1844."

Net Annual Consumption of Soap in Great Britain, for which duty was paid.

1829—30,367,262	}	Average consumption 100,605,850 lbs.; Duty 28 <i>l.</i> per ton.
1830—109,377,918		
1831—97,296,726		
1832—101,231,295		
1833—Duty reduced.		
1834—115,635,967	}	Average consumption 118,902,631 lbs.; Duty 14 <i>l.</i> per ton.
1835—123,163,968		
1836—117,887,639		
1837—113,163,182	}	Average consumption 119,542,150 lbs.; Duty 14 <i>l.</i> per ton.
1838—127,040,637		
1839—118,422,612		
1840—121,044,787		
		Average consumption 128,164,991 lbs.;
1841—122,863,105	}	Duty 14 <i>l.</i> 14 <i>s.</i> per ton. There are good reasons for attributing this considerable increase entirely to the increased vigilance of the Excise.
1842—125,287,058		
1843—136,344,811		

An Estimate of the actual Quantity of Soap used in Great Britain.

According to the Excise Returns, the quantity of soap now used in England per head, per annum, is 7.21 lbs.

The following statements of the quantity of soap used by different classes of society, derived from authentic sources, it is believed, may be relied on:

- | | |
|---|----------|
| 1. The average consumption per head in work-houses is for each inmate per annum | 7 |
| 2. Convicts are allowed each per annum | 11 |
| 3. All estimates of the expenditure of the poor agricultural population allow for families earning 10 <i>s.</i> per week and under, each per annum (Or $\frac{1}{2}$ lb. per week for a family of five or six persons.) | 4 |
| 4. Extensive inquiries prove that labourers earning from 10 <i>s.</i> to 30 <i>s.</i> per week, use each per annum from | 10 to 12 |
| 5. Shopkeepers and tradesmen per annum from | 12 to 15 |
| 6. And the wealthier classes per annum from | 15 to 30 |

By dividing the population into three classes, and assuming the minimum quantities as the consumption of each class, an estimate of the actual quantity of soap used may be formed.

1. Agricultural labourers, and others, earning 10s. per week, and under, whose consumption is estimated at only $\frac{1}{2}$ lb. per week for a family of six ; or 4 lb. each per annum .	}		lbs.
		7,500,000 at 4 lbs. =	30,000,000
2. Well - paid workmen, and small shopkeepers, allowed for each member of the family 10 lbs. per annum .	}		
		7,500,000 at 10 lbs. =	75,000,000
3. All the middle and upper classes, allowed for each person 15 lbs.	}		
		3,897,463 at 15 lbs. =	58,461,945

Census of 1841, and 2 per cent. increase since that time .	}	18,897,463	163,461,945

Actual quantity charged with duty by the Excise .		136,344,811
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Unaccounted for, either displaced by substitutes paying no duty, or by illicit trade .	}		27,117,134

This estimate, though evidently far under the real consumption, proves there is still a large amount of illicit trade ; and there can be no doubt but that by reducing the price of soap to $2\frac{1}{2}d.$ or $3d.$ per lb., the quantity used would materially increase.

The average consumption of soap in Jersey, where it is free of duty, is estimated at 13·1 lbs. for each person per annum. The estimate for the population of the Isle of Man, where soap is also free of duty, is 8·68 lbs. for each person.

Comparison of the progress of the Consumption of Soap with that of other articles and the population, from 1831 to 1841.

	Per cent.
Increase of population	14·5
„ houses	18·6
Increase of consumption of—	
„ paper	54·7
„ timber	36·0
„ iron	40·08
„ cotton	62·0
„ flax	45·5
„ soap <i>only</i>	26·0
though the duty was reduced one-half in 1833.	

Arguments against the Soap Duty.

1. The extra cost of soap in consequence of the Excise regulations gives to the Foreign over the English manufacturer an advantage of $8\frac{1}{2}$ per cent. in the case of tallow soap, and $4\frac{3}{4}$ per cent. in the case of palm-oil soap. To the Irish manufacturer the advantage is about 10 per cent. on the quality usually exported.

2. The restrictive regulations exclude the trade, by reason of the limitation as to the sizes of the bars,—the specific gravity of the soap,—and the mode of manufacturing,—from many foreign markets.

3. There is no duty on soap in Ireland.

4. One-fourth of the duty collected is returned in drawbacks.

5. Soap manufacturers duly licensed and surveyed cannot make fancy or perfumed soap, nor under the Excise laws conduct their works in the most economical manner.

6. The great benefit the poor would immediately derive from its repeal, by which the price of good soap would be reduced from $4\frac{1}{2}d.$ and $5d.$ to $3d.$ per lb.

7. Soap manufacturers are nearly unanimous in their application for the repeal of the duty and relief from Excise regulations, whilst the vast majority of the glass and paper manufacturers wish their respective duties to be retained.

SULPHUR AND SULPHURIC ACID.

§ I. Sulphur.—II. Sulphurous Acid.—III. Sulphuric Acid.

THE extensive applications of sulphuric acid have long caused this substance to be ranked among the most important of the objects of chemical manufacture. Whenever any process in the arts requires the introduction of an acid, the particular nature of which is indifferent, as is frequently the case, sulphuric acid, from its relative inexpensiveness, is usually preferred before all others; and if accidental circumstances should render its introduction in such a case inadmissible, it generally becomes a grand object of the manufacturer so to modify the process as to overcome the impediment to its application. In fact, so numerous and important are the applications of this acid in the arts, that it has been justly observed that the commercial prosperity of a country may be fairly estimated from the amount of sulphuric acid it consumes. In energy, it surpasses all other acids, being capable of liberating most of them from their combinations with bases by virtue of its superior affinity for the base, and hence it becomes the key to the preparation of almost all other acids.

Pure sulphuric acid, of which the oil of vitriol of commerce is a hydrate, or compound of with water, is a combination of sulphur with oxygen; and one of a series of six such bodies, all of which possess the properties of acids. Before considering in detail the

properties of and mode of manufacturing sulphuric acid, it will be proper to advert briefly to its elementary basis, sulphur, and to one of its acid compounds with oxygen, namely, sulphurous acid.

§ 1. SULPHUR.

Anciently, the name of sulphur was made use of to designate a variety of substances possessing very little resemblance to each other. M. Macquer, one of the most celebrated French chemists of the eighteenth century, observed that no name in chemistry had been so extensively applied and so much abused as that of sulphur. It was made use of to designate all inflammable substances, as vegetable and animal oils and fats, resins, bituminous matters, and a supposed principle of inflammability afterwards called "phlogiston," which was erroneously believed to exist in all inflammable bodies. But the name was not even confined to inflammable matters, for some of the alchemists make mention of a sulphur which is incombustible. The body now called sulphur, which has been known from time immemorial, was classed with bitumens. Towards the close of the seventeenth century, the name was exclusively applied to the elementary body which now possesses it, the difference in the various substances confounded together under that name having been previously demonstrated by Beccher and his pupil Stahl.*

* The views of Beccher and Stahl, however, on the nature of sulphur, were far from correct. They considered it to be a compound body, consisting of sulphuric acid or sulphurous acid united with phlogiston, or the principle of inflammability. They observed that sulphur, when

- In the free state, or combined with metals as sulphurets, or with metallic oxides as sulphates, sulphur forms an abundant constituent of mineral substances, confined to no particular geological formation, occurring in rocks which possess the greatest dissimilarity, and found in beds, in veins, and diffused through the mass of a rock. The commercial demands for this article are supplied from two sources, the native or free sulphur, and metallic sulphurets, especially iron pyrites.

Native sulphur abounds in the vicinity of active volcanoes, from which it is exhaled in large quantities, and condenses in *fissures* forming sulphur veins. In the plain of the Solfatara near Vesuvius, a very considerable deposit of sulphur is found in fissures in lava. In a few localities, namely, Quito in Peru, Suabia, and near Schemnitz in Hungary, sulphur is met with in veins traversing gneiss and mica slate. It is found most abundantly, however, in *beds*, accompanied by gypsum, and also, frequently, by sulphate of strontian, in splendid crystals. In Sicily, from whence

burned in the air, may be entirely consumed without leaving ashes, or yielding soot, but with the production of an acid vapour highly irritating to the lungs, and susceptible of condensation by water; and that this vapour is the only product of the combustion which can be collected. It was hence concluded that the constituent parts of sulphur are the volatile acid and the phlogiston also developed in the combustion, as heat and light; and one chemist, Neumann, even went so far as to determine that sixteen ounces of pure sulphur contain fifteen ounces and three quarters of acid, and a quarter of an ounce of phlogiston. These views of the nature of sulphur obtained the general assent of chemists until the chemical revolution which took place about 1777, when it was shewn that this body must be considered a simple substance, it being undecomposable by any of our present instruments of analysis. The acid product of its combustion was shewn to be formed through the union of the sulphur with the oxygen of the air, its weight always exceeding that of the sulphur consumed, instead of being inferior in weight, as the phlogiston theory previously entertained required.

almost all the native sulphur brought to this country is procured, it occurs in beds of a blue clay formation, considered by Dr. Daubeny to be coeval with the gypsum bed of Paris, extending inwards from the south coast of the island to the district of Etna. It also occurs in beds of indurated marl and compact limestone. Lastly, sulphur is still being constantly evolved from Etna, Vesuvius, and the volcanoes of Iceland, Guadaloupe, and South America.

Native sulphur, when pure, as it generally is if merely separated carefully by mechanical means from the accompanying earthy substances, is brittle, translucent, and possessed of considerable lustre when freshly fractured. Its colour is yellow, varying a little in tint from bright citron colour to greyish yellow. It is found massive, pulverulent, cellular, stalactitic, in rounded masses, and frequently in large regular crystals of various modifications of the rhomboidal octohedron. The crystals brought from Sicily are the most perfect, and sometimes measure four inches in length. The fracture of the crystals is fine-grained, and usually conchoidal, but sometimes splintery. The specific gravity of native sulphur is 2.072. According to Stromeyer, the orange-red colour of some specimens of native sulphur proceeds from the presence of a minute quantity of a compound of sulphur with silenium, and not from iron or realgar as is generally supposed.

The only impurity commonly contained in native sulphur, when carefully separated by mechanical means from the accompanying foreign substances, is a small quantity of earthy matter, which may be got rid of with facility by the process of sublimation or distil-

lation. Sulphur being volatile, and the earthy matters fixed, the former distils over at a high temperature, leaving the impurities behind. The distilled sulphur is then melted, cast into moulds, and sent to the market.

The native sulphur procured from a few sources, Solfatara for instance, is very intimately mixed with a considerable portion of earthy substances, the mechanical separation of which would be almost impossible. Such ore is broken into small fragments of the size of a walnut, and put into earthen jars arranged in a double row along a furnace; the jars are covered with earthenware lids, and a bent earthen pipe about two inches in diameter is adapted to each lid; the other end of the pipe dips into another earthen covered jar with a hole through its bottom, standing over water. On the application of heat, the sulphur volatilizes and passes through the pipes into the receivers, where it congeals. The products of several distillations having been collected, the contents of the receivers are melted together, when the impurities either rise to the top and may be skimmed off, or subside to the bottom. The sulphur is afterwards cast into moulds for sale.

Sulphur may be obtained in almost unlimited quantities from iron pyrites, or the bisulphuret of iron, which exists in immense quantities in nearly all metaliferous rocks. When pure, this mineral contains 32 parts of sulphur and 28 parts of iron. If heated in a proper distillatory apparatus without access of air, it parts with exactly one-half of its sulphur, which may be collected in a suitable condensing vessel, and the protosulphuret of iron remains behind, consisting

of 16 parts of sulphur and 28 parts of iron.* If, however, air is allowed to have free access, or if the mineral is roasted instead of being heated in a distillatory apparatus, the whole of the sulphur is consumed, becoming converted into sulphurous acid gas; and oxide of iron, instead of protosulphuret of iron, is the residue.

When the distillation of iron pyrites is conducted carefully on the small scale, the ore may be made to afford from 25 to 27 per cent. of sulphur, but on the large scale it rarely yields more than 16 per cent. The protosulphuret which remains behind readily becomes converted into copperas when moistened and exposed to the air.

Copper pyrites, which usually consists of about equal parts of sulphuret of copper and sulphuret of iron, may also be made available as a source of sulphur, in the same manner as iron pyrites, and the residue may be used for smelting. A considerable quantity of sulphur was formerly obtained in this way from the copper ore raised at the Parys mine at Anglesea.

The sulphur procured from pyrites is never so pure as that got by distilling native sulphur. Besides earthy impurities, the former generally contains a considerable quantity of arsenic, a substance from

* A process of this kind for obtaining sulphur from iron pyrites has long been worked at Goslar and Fahlun in Sweden, but the apparatus employed in the process admits air so freely, that nearly all the sulphur is consumed; not more, it is said, than two parts of sulphur being obtained from one hundred of the ore. In Bohemia and Saxony, the iron pyrites is heated in large earthenware pipes, arranged in a furnace or gallery; the evolved sulphur flows into pipes containing cold water, on the outside of the furnace.

which iron pyrites, and especially that found associated with copper pyrites, is never entirely free, while the sulphur imported from Sicily rarely contains even a trace of arsenic. This impurity exists in the pyrites, in the form of arseniuret of iron, and in the sublimed sulphur, as orpiment or realgar, which are sulphurets of arsenic. The freedom of sulphur from these and some other impurities, particularly silica, oxide of iron, sulphuret of iron, carbonate of zinc, and sulphate of zinc, may be tested by its solubility in boiling oil of turpentine. If pure, sulphur completely dissolves in ten times its weight of that liquid, at the boiling point; but the impurities remain undissolved, and may be collected on a filter and weighed. The sulphur formerly obtained at Anglesea left one-fifteenth of its weight of insoluble matters, consisting chiefly of orpiment (Aikin). Good Sicilian sulphur, when thus treated, seldom leaves more than three per cent. of insoluble residue, which is an earthy substance quite free from arsenic.

A mode of obtaining sulphur has been patented by Mr. Duclos, of Swansea, which might possibly be turned to profitable account in some establishments, where the smelting and calcination of metallic ores are conducted. It consists in mixing in such a leaden chamber as that employed in the manufacture of sulphuric acid, two volumes of sulphuretted hydrogen gas with one volume of sulphurous acid gas, a quantity of steam being at the same time admitted into the chamber. The hydrogen of the sulphuretted hydrogen gas unites with the oxygen of the sulphurous acid, and the sulphur of both is precipitated in the solid state. Sulphurous acid is an abundant bye-pro-

duct of the calcination of metallic ores, in the process of smelting; and sulphuretted hydrogen, if not otherwise afforded as a bye-product, may be obtained by acting on metallic sulphurets with muriatic acid. Another method of obtaining sulphuretted hydrogen, proposed by Mr. Duclos, is a part of a process for obtaining carbonate of soda from sulphate of soda. The sulphuret of sodium obtained by calcining the sulphate with coal is dissolved in water, and through the solution contained in a series of Woulf's bottles is transmitted carbonic acid gas. The sulphuret of sodium is thereby decomposed, with formation of carbonate or bicarbonate of soda, and evolution of sulphuretted hydrogen gas. Mr. Duclos obtained his patent in July, 1839.

A somewhat similar process has been made the subject of a patent by Mr. Dyar and Mr. Chisholm (obtained June, 1839), in which the sulphurous acid is decomposed by free hydrogen. The former is obtained in the usual manner by the calcination of pyrites or other metallic sulphuret, and the latter in a state of mixture with carbonic oxide by passing steam over burning coke. The calcination of the sulphuret and the combustion of the coke are conducted in two adjoining fire-places or flues, communicating with each other at top, where the mixture of the gases takes place. The communication between the two flues must be sufficiently near to the burning flue to keep the temperature of the gases still elevated. A flue leads from the middle of this junction into a large chamber to receive and condense the sulphur. When pyrites is the sulphuret employed in this process, it is preferred to separate a portion of its sulphur first by

distillation, and to calcine the residuary protosulphuret for the production of sulphurous acid gas, as above described.*

In a state of purity, sulphur is perfectly tasteless, and at common temperatures, inodorous, but by friction it acquires a slight fœtid smell, and becomes electrically excited, having the power of attracting

* The crude sulphur obtained by any of the methods which have just been described, is refined in one of two ways : by a simple fusion, when some of the foreign matters settle to the bottom, and others rise to the top, or by subjecting the sulphur to a second distillation. When the only impurity is earthy matter or mineral powders, the first method suffices. The sulphur is melted in a cast-iron pot, the impurities on the surface are skimmed off, and the sulphur is transferred to a copper vessel moderately heated ; from the latter it is poured into wooden moulds. The fire should not be allowed to have free access to the bottom of the melting-pot employed in this operation, but be made to play only around its middle zone. The subsidence of the impurities is found to be considerably facilitated by this precaution.

Sulphur procured by the distillation of pyrites can only be properly refined by subjecting it to a second distillation. This operation is generally conducted in iron retorts, the beaks of which terminate in a large chamber, where the sulphur condenses in the solid or liquid state, according to the temperature. This operation is conducted on a very extensive scale at Rouen and at Marseilles. The condensing chamber at Marseilles is about twenty-three feet in length, eleven feet in width, and thirteen feet in height ; and the iron retorts, of which there are two to one chamber, are about three feet in diameter, and twenty-two inches in depth. Each retort being charged with about eight hundredweight of crude sulphur, a gentle fire is applied first to one retort, and three hours afterwards to the other. The doors and all apertures in the chamber are closed with a lute of loam. The heat should be moderate at first to prevent the sulphur from boiling over into the chamber, but after a short time it may be increased without inconvenience. The retorts are charged afresh four times a day, and the distillation is continued without interruption for a week. During the first day or two the sulphur condenses in the solid state, as *flowers of sulphur*, but the temperature of the chamber usually becomes too high about the third day for the sulphur to solidify ; it then flows down in the liquid

light bodies in its vicinity. If a roll of sulphur is held in the warm hand, it breaks across with a particular crackling noise, and the hand acquires a disagreeable odour, which lasts for a few minutes. The fracture of the sulphur by the heat of the hand arises from the imperfect conducting power of the sulphur; the exterior and expanded part of the roll being unable to conduct the heat quickly to the interior for that to be expanded in like degree; the break-

state to the floor of the chamber, from which it is drawn off through two iron pipes, and conducted into wooden moulds, slightly conical, where it acquires the form of the cylinders known in commerce under the name of roll-sulphur. About four hundredweight may be distilled from one pot in twenty-four hours. The chamber is supplied with an opening and a valve at its top, to give vent should any explosion take place within, of which there is a possibility before the chamber becomes filled with sulphur vapour; but not after all the air is expelled, unless the temperature is allowed to fall and the air re-enter.

An arrangement has been lately adopted which has considerably reduced the chance of explosion, by causing a more uniform temperature, and thus preventing the ingress of air. Above the retort in which the distillation is conducted, a large cistern is so placed as to be exposed to the waste heat of the fire, and into this cistern is introduced the crude sulphur to supply the retort. A tube furnished with valves is made to wind round the cistern, and to conduct the liquid sulphur to the retort underneath. By this arrangement a more rapid distillation is effected, as well as a more uniform temperature in the chamber, and the loss, which in the ordinary method generally amounts to about 20 per cent., is reduced to 12 per cent.

Sulphur is obtained in the form of flowers of sulphur by conducting the vapour from the retorts into a chamber the temperature of which is kept below the fusing point of sulphur. The chamber for this purpose is considerably larger than that in which the sulphur is condensed in the liquid state, and the operation is conducted much more slowly. In this state, sulphur is of a pale yellow colour, and when examined by the microscope is found to be composed of minute crystals. As met with in commerce, this form of sulphur is not quite so pure as roll-sulphur, as it is always impregnated with a little sulphurous or sulphuric acid. These acids, however, may be easily removed by washing with hot water, as directed for certain pharmaceutical purposes.

ing of a thick glass vessel on the sudden application of heat proceeds from the same cause. Sulphur is very brittle and easily reduced to powder.

The colour of the sulphur met with in commerce is of different shades, according to the temperature to which it had been subjected in the process of distillation. It is sometimes greenish-yellow, sometimes bright yellow, and sometimes brownish-yellow. The first had been exposed to a lower temperature than the second, and the second to a lower than the third.

When made to pass slowly from the fluid to the solid state, sulphur may be obtained in the form of distinct crystals. One method of procuring the crystals is to fuse a considerable quantity in a ladle or crucible and allow it to cool gradually. As soon as the surface is solidified, it is punctured, and the sulphur which still remains in the fluid state poured out; the cavity in the crucible or ladle is then found entirely lined with distinct needle-shaped crystals. It is remarkable that the form of the crystals thus obtained is wholly different from that of native sulphur, belonging, in fact, to another system of crystallization. The crystals formed in the manner described are modifications of an oblique prism with a rhomboidal base, but the crystals of native sulphur are elongated octohedrons, with a rhomboidal base. By other artificial processes, however, in which the sulphur is deposited from the vaporous or liquid state at a temperature inferior to that at which it solidifies in the above experiment, crystals may be obtained of the same shape as native sulphur. Thus solutions of sulphur in oil of turpentine, chloride of sulphur, and bisulphuret of carbon, deposit such crys-

tals on cooling or on evaporation, and the minute crystals which comprise flowers of sulphur have also the same shape as the crystals of native sulphur. From being capable of assuming these two different crystalline forms, sulphur is said to be *dimorphous*.*

* The most remarkable and peculiar property of this element is exhibited in the appearances which it assumes in the liquid state at different temperatures, first observed by M. Lecat, a celebrated French surgeon, about the middle of last century. When sulphur is heated to a temperature near 234° Fahr., it fuses, forming a very thin liquid, quite transparent and of a citron colour, or if not heated above its fusing point, almost colourless. On being allowed to cool, it crystallizes into yellow needles, transparent, but which soon become opaque and friable.

If, instead of allowing the melted sulphur to cool, the heat be gradually increased, it becomes deep yellow and translucent; whereas, before, it was perfectly transparent. Moreover, on increasing the temperature to a point between 480° and 500° Fahr., it undergoes another change, assuming a deep reddish-brown colour, and what is very remarkable, increases in consistency, becoming at last so firm that the containing vessel may be inverted without the sulphur flowing out.

If heated still higher, the sulphur again becomes liquid, but retains its dark colour. At about 788° Fahr. (according to Frankenheim) it enters into ebullition, giving off an orange-coloured vapour, which condenses on coming in contact with a cold body as a very fine powder. On being allowed to cool from its boiling point down to its freezing point, all the changes which have been described may again be witnessed, and the same specimen of sulphur may be employed for any number of experiments.

A curious fact connected with these changes is, that if the sulphur while in the thick state is suddenly cooled by immersion in cold water, it remains soft, transparent, and retains its dark colour for some time after it is perfectly cool, but these characters are not permanent. In this state, sulphur is sufficiently ductile to admit of being drawn into fine threads of several feet in length. But if fluid sulphur near the melting point is treated in precisely the same manner, it immediately becomes quite solid, friable, opaque, and possessed of its usual yellow colour.

It is inferred from these remarkable appearances that liquid sulphur is capable of existing in at least three different physical states. M. Frankenheim, who has lately been occupied in investigating this interesting subject, designates the three varieties of sulphur by the symbols S_α , S_β , and S_γ . S_α is the colourless variety obtained at a low tem-

When sulphur is heated in the open air to about 600° Fahr., it undergoes a low combustion, with the developement of a pale blueish flame, and formation of sulphurous acid, which is a gaseous body possessed of a disagreeable and extremely pungent odour.

perature ; $S\beta$ is the deep yellow sulphur obtained at a higher temperature ; and $S\gamma$ the dark brown semi-fluid variety formed between 480° and 500° Fahr. The most important observation made on this subject by M. Frankenheim, is that the conversion of one variety into another does not take place in a gradual manner, but immediately and at a constant temperature. If the sulphur is heated in such a manner as to admit of being viewed by the microscope while undergoing the changes, as between two small plates of glass, a perfect line of demarcation is perceptible between the different sulphurs, shewing the change to take place immediately from one to another. On observing the indications of the thermometer during the succession of these appearances, it was found that the temperature rises gradually to a point between 480° and 500° Fahr., but then remains stationary until the $S\beta$ is entirely converted into $S\gamma$, when it again rises, going up steadily to 788°, which is the boiling point of sulphur. Further, on cooling, the thermometer falls gradually until at the point between 480° and 500° ; then remains for a time stationary, or nearly so, and afterwards continues to descend regularly. These observations fully prove that heat becomes latent during the passage of $S\beta$ to $S\gamma$; that is, $S\gamma$ contains caloric in some peculiar state of combination, not manifest, but in a hidden state, which is not contained in $S\beta$.

MM. Marchand and Scherer have lately determined the density of the soft sulphur obtained by pouring $S\gamma$ into cold water to be 1.959. As it becomes hard its density rises to 1.98, and when it acquires the yellow colour its density is 2.041. Sulphur, in its ordinary state, that is after having been melted and allowed to become yellow again (S_a), has the density 2.043.

Although sulphur does not boil before it attains the temperature 788° Fahr., yet it gives off vapour at much lower temperatures, even before it attains its melting point. It is hence believed that each of the three varieties of sulphur has its proper vapour ; and that the three vapours differ from each other in density, as the three fluid sulphurs differ in physical appearances : this is a subject, however, which requires, and certainly well deserves, further investigation.—(M. Frankenheim's original paper on this subject may be found in the *Journal für Practische Chemie*, xvi. 1 ; an account of it is given by Berzelius in his *Rapport Annuel*, 1841.)

This product consists of a combination of sulphur with oxygen derived from the atmosphere; its volume is the same as that of the oxygen consumed in the combustion. The heat produced by the low combustion of sulphur in the air must be very inconsiderable, for all the sulphur in a small quantity of gunpowder may be burned away, with care, without producing explosion. The combustion of sulphur in pure oxygen gas, which is also attended with the formation of sulphurous acid, is much more vivid than in air. When sulphur is burned in air or oxygen in contact with water or aqueous vapour, it combines with an additional dose of oxygen, thus producing sulphuric acid; but the quantity of that acid formed in such circumstances is always very inconsiderable.

Sulphur may be made to combine with all metals, forming a class of substances called *metallic sulphurets*. Many of the sulphurets of metals proper are found in nature, and these compounds frequently constitute the most available sources of their metallic bases. The affinity of sulphur for metals generally is very intense, exceeding that of oxygen. When a mixture of iron or copper filings with flowers of sulphur, contained in a Florence flask, is heated pretty strongly at one part, the sulphur and metal presently unite, with the developement of a very intense heat, which causes the union to take place throughout the whole mixture. The metal strictly burns in the vapour of sulphur, just as iron may be burned in oxygen gas.

Sulphur is insoluble in water and in cold alcohol. If, however, both sulphur and alcohol are brought

together in the form of vapour, an alcoholic solution of sulphur may be condensed, from which the sulphur is precipitated on the addition of water. At all common temperatures water is without action on sulphur, but steam is partly decomposed by melted sulphur with the formation of a small quantity of an inflammable gas, probably sulphuretted hydrogen.

When sulphur is boiled in solutions of the caustic alkalies, red liquids are formed, which contain a large quantity of sulphur in chemical combination with the alkali. On the addition of an acid, the alkaline sulphuret is decomposed, and a white precipitate is formed, consisting of sulphur in combination with a small proportion of water.

By far the most considerable applications of sulphur are in the preparation of sulphuric acid and of gunpowder, which is a mixture of sulphur with charcoal and nitre. A great quantity is consumed in making common brimstone matches, lucifer matches,* congreves, and artificial fire-works; it is also employed in medicine, in the preparation of vermilion, which is a compound of sulphur and mercury, to cement iron bars into stone, and for the purposes of bleaching and disinfecting. The two applications last mentioned are, however, applications of sulphurous acid produced by the combustion of sulphur.

The consumption and price of sulphur have been

* According to a recent estimate, the annual consumption of lucifer matches in Great Britain is about 5,000,000,000. A thousand pounds' worth of pine per annum is regularly imported from America by a single manufacturer.

greatly affected within the last few years by an impolitic and fortunately unsuccessful attempt of the Neapolitan Government to establish a monopoly in the sulphur trade of Sicily. The project originated with a Frenchman, M. Taix, who, in 1836, laid a plan before the Neapolitan Government for establishing a company which was to enjoy the exclusive right of purchasing Sicilian sulphur at fixed prices during ten years, on the condition of expending a certain sum of money in constructing roads and exporting one-third of the quantity produced in Sicilian ships. At that time the consumption of sulphur in Great Britain was about thirty-two thousand tons per annum, nearly all of which was procured from Sicily; for, although native sulphur might be procured from Iceland, St. Vincent's, Teneriffe, and other volcanic districts, the expense of procuring it from Sicily was considerably less than from any other place.

In the autumn of 1838 the Sicilian monopoly was commenced, and the immediate consequence was a rise in the price of sulphur from 6*l.* or 7*l.* to 13*l.* or 14*l.* per ton. In 1839 the importation of sulphur into Great Britain fell from forty-four thousand tons (the amount in 1838) to twenty-two thousand tons, of which only five thousand four hundred were procured direct from Sicily. Through the interference of the British Government, however, the monopoly was abolished in the summer of 1840, and the sulphur trade placed on the same footing as previous to 1838, in which state it still continues. In 1820 the consumption of sulphur in Great Britain amounted to no more than five thousand tons.

During the year 1842, the exportation of sulphur

from Sicily to different countries was as follows. To Great Britain, 14,214 tons; to France, 11,010 tons; to Austria, 3,231 tons; to the United States, 2,834 tons. The average price of sulphur at Sicily was 2*l.* 13*s.* per ton, exclusive of the export duty.

While the monopoly existed, a cargo of sulphur was brought to this country from Iceland, and iron pyrites was then introduced very extensively as a source of sulphur in the manufacture of sulphuric acid. This application of pyrites is still very general, and likely to continue so, notwithstanding the abolition of the monopoly; a consequence of which is, that the quantity of sulphur at present imported into Great Britain from Sicily is less than one half of the amount imported in 1836.*

* "Reflecting upon the important influence which the price of sulphur exercises upon the cost of production of bleached and printed cotton stuffs, soap, glass, &c., and remembering that Great Britain supplies America, Spain, Portugal, and the East with these, exchanging them for raw cotton, silk, wine, raisins, indigo, &c., we can understand why the English Government should have resolved to resort to war with Naples, in order to abolish the sulphur monopoly, which the latter power attempted recently to establish. Nothing could be more opposed to the true interests of Sicily than such a monopoly; indeed, had it been maintained for a few years, it is highly probable that sulphur, the source of her wealth, would have been rendered perfectly valueless to her. Science and industry form a power to which it is dangerous to present impediments. It was not difficult to perceive that the issue would be the entire cessation of the exportation of sulphur from Sicily. In the short period that the sulphur monopoly lasted, fifteen patents were taken out for methods to obtain back the sulphuric acid used for making soda. Admitting that these fifteen processes were not perfectly successful, there can be no doubt that it would ere long have been accomplished. But then in gypsum (sulphate of lime), and in heavy spar (sulphate of barytes), we possess mountains of sulphuric acid; in galena (sulphuret of lead), and in iron pyrites, we have no less abundance of sulphur. The problem is how to separate the sulphuric acid or the sulphur from these native stores. Hundreds of thousands of pounds' weight of sulphuric

The composition of all the known compounds of sulphur and oxygen, including those recently discovered by M. Langlois and MM. Fordos and Gelis, is expressed by the symbols following :

Hyposulphurous acid	$S_2 O_3$
Bisulpho-hyposulphuric acid (the tetrathionic acid of Berzelius)	$\} S_4 O_6$
Sulpho-hyposulphuric acid (the trithionic acid of Berzelius)	$\} S_3 O_6$
Sulphurous acid	$S O_2$
Hyposulphuric acid	$S_2 O_3$
Sulphuric acid	$S O_3$

The only one of these compounds which can be formed by the direct union of sulphur and dry oxygen is sulphurous acid; for which reason, and also because the study of the more important sulphuric acid will be greatly facilitated by a previous acquaintance with sulphurous acid, we shall, in the next place, briefly consider the properties and some applications of the latter.

§ II. SULPHUROUS ACID.

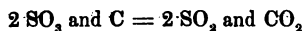
When sulphurous acid gas is required for purposes in the arts and for disinfection, in which cases its absolute purity is not essential, nothing can be simpler than the mode of preparing it. Sulphur is put

acid were prepared from iron pyrites, while the high price of sulphur consequent upon the monopoly lasted. We should probably, ere long, have triumphed over all difficulties, and have separated it from gypsum. The impulse has been given, the possibility of the process proved, and it may happen in a few years that the inconsiderate financial speculation of Naples may deprive her of that lucrative commerce."—Liebig's *Familiar Letters on Chemistry*.

into an iron or earthen pot and set on fire; the pot is placed either in a close chamber, in which the articles to be exposed to the acid are suspended; or else in a sort of stove, where the means of producing a proper current of air over the burning sulphur, and of conducting the sulphurous acid into the chamber where it is required for use, are at the command of the operator.

If required in a state of purity, and only in small quantities, sulphurous acid gas is most readily obtained by withdrawing from sulphuric acid a portion of its oxygen; for which purpose either metallic mercury or copper may be conveniently employed. The metal acquires one-third of the oxygen of one portion of the acid; the remaining oxygen and the sulphur of that portion of acid come off as sulphurous acid, while the metallic oxide unites with another portion of sulphuric acid without decomposition, thus forming a sulphate.

Concentrated sulphuric acid is decomposed by carbon and carbonaceous substances in a somewhat similar manner, but the sulphurous acid gas obtained in this way is always accompanied with a large proportion of carbonic acid, the source of which will be obvious by the following equation expressive of the reaction which occurs between two equivalents of sulphuric acid and one equivalent of carbon:



The principal uses of sulphurous acid in an experimental laboratory are for the preparation of the aqueous solution of the gas and of alkaline sulphites, for which purposes the admixture of carbonic acid gas

with the sulphurous acid is immaterial. A convenient form of apparatus to be used in preparing sulphurous acid by means of oil of vitriol and charcoal is represented in the annexed figure. Seven or eight ounces by weight of oil of vitriol (a quantity equal in volume to about four ounces by measure of water), and half an ounce of finely powdered charcoal, are introduced into the flask and well mixed by agitation. On the application of heat to the flask, a gaseous mixture of sulphurous acid and carbonic acid is disengaged,

Fig. 34.



which is conducted in the first place through a bottle *a*, containing about an ounce of water, and afterwards, if a solution of sulphurous acid is required, into the bottle *b*, or if the gas itself is wanted, the exit-tube of the intermediate bottle may be led to the mercurial trough or elsewhere. Affixed to the cork of the bottle *b* is a stout tube open at both ends, through which passes the exit-tube of the flask, fitting loosely. The use of this bottle is to intercept any

sulphuric acid vapour or the materials in the flask, if projected by ebullition, and also to prevent the liquid in the bottle *b* from entering the flask, should a contraction occur in that flask from cooling.

Sulphurous acid is always being exhaled from the earth in considerable quantity in the vicinity of active volcanoes, with the occasional exception, according to M. Boussingault, of the volcanoes of equatorial regions.*

Although gaseous at all common temperatures and pressures, sulphurous acid is not a permanent gas. When exposed to a pressure of little more than two atmospheres, or when passed through a tube surrounded by a freezing mixture of ice and salt, it assumes the liquid form. In this state it is quite limpid and colourless; it has the specific gravity 1.45, and boils at 14° Fahr. By evaporation, this, like all other very volatile liquids, generates a great degree of cold; on which account it was formerly employed to freeze mercury, and to liquefy some gases which were considered permanent. For this purpose, however, liquid sulphurous acid has given place to solid carbonic acid. Sulphurous acid is readily absorbed by water, and the solution possesses the pungent odour of the gaseous acid. At 60°, water is capable

* The quantity of sulphurous acid exhaled from volcanoes is said to be greater after than before an eruption. The disengagement of this gas from the hill of Solfatara is very considerable and constant, so as to render the unguarded approach to the hill extremely dangerous. The inhalation of air merely tainted with sulphurous acid speedily produces the most distressing irritation of the lungs, and at length asphyxia and death. The death of Pliny the Elder was produced from such a cause, he having incautiously approached too near the crater of Vesuvius at the time of the famous eruption which overwhelmed Pompeii and Herculaneum.

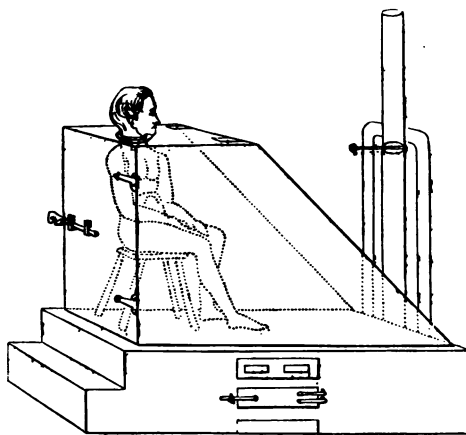
of dissolving 37 times its volume of the gas; hence, when the acid is required in a gaseous state, it must not be collected over water, but over mercury, which is without action on the gas. Sulphurous acid gas contains two volumes of oxygen and one-third of a volume of sulphur vapour condensed into two volumes. By weight it consists of 16 parts, or 1 eq. of sulphur, and 16 parts or 2 eqs. of oxygen. When a little water is brought into contact with the liquid acid, a crystalline hydrate is formed containing 20 per cent. of acid, corresponding to $\text{SO}_2 + 14\text{HO}$. If pure, sulphurous acid may be passed through a red-hot tube without undergoing any change; but if in contact with combustible matters, such as carbon, potassium, sodium, and hydrogen, it is decomposed at a red heat with separation of sulphur. The density of sulphurous acid is 2216, the air being considered 1000.

Sulphurous acid gas has long been employed in the French hospitals in the treatment of cutaneous diseases. The use of this gas as an external remedial agent was suggested by Glauber so long ago as the year 1659. Very simple and inexpensive apparatus have been contrived to apply the gas, one of which is figured in the annexed cut. It represents a box of wood placed over a small fire-place, in which the sulphur is burned in such a manner that the vapour enters and fills the box. The top of the box is provided with a hole through which passes the head of the patient, the escape of gas being prevented by folding a wet cloth around his neck.

As sulphurous acid destroys the colour of many vegetable and animal substances, the vapour from

burning sulphur is often made available in certain bleaching operations, particularly in the whitening of

Fig. 35.



woollen goods, silk, and straw. Very few vegetable colouring matters resist the action of sulphurous acid, but cochineal and some other animal colouring matters are scarcely at all affected by it. The chemical nature of the bleaching action of sulphurous acid is different from that of chlorine. The latter generally acts either by abstracting hydrogen from, or by imparting oxygen to, the colouring matter; but sulphurous acid produces neither of these effects. Chlorine, when applied in sufficient quantity to bleach perfectly, always effects a complete decomposition of the colouring matter, so that the latter is not reproducible, so far as yet known; but the colours of substances bleached by sulphurous acid may generally be restored, unless the action has been prolonged for a considerable time by the application of an alkali, a stronger acid, or, if an excess of sulphurous acid remains, by

mere exposure to the air. As a bleaching agent, sulphurous acid seems to act generally by abstracting a portion of the oxygen of the colouring matter, which becomes reduced to its colourless basis. Silks and woollen goods to be bleached by this process are suspended in a damp state on strings across a chamber, in the corners of which are placed braziers of burning sulphur. The chamber should be provided with a flue and damper, and all the crevices around or in the door should be stopped up with wet clay during the "sulphuring;" one small aperture only being left, the means of contracting which are at the command of the operator. A little more than two pounds of sulphur is generally required for one hundred pounds of silk.

Sulphurous acid is also employed to blanch isinglass; to remove fruit-stains from linen, &c.; to disinfect an unwholesome atmosphere, garments, bed-clothes, &c.; to kill moths and other destructive insects; to prevent too rapid fermentation in wine-vats; and to impregnate casks in which wine, beer, and other fermented liquors are to be preserved, with a view of preventing the acetous fermentation.

§ III. SULPHURIC ACID.

The earliest notice of sulphuric acid which is known to exist, is in the writings of Basil Valentine, a celebrated alchemist of Erfurt, and monk of the Benedictine order, who wrote in the former part of the fifteenth century. The Swiss alchemist Paracelsus, and Agricola, a German physician, also make sufficient

allusions to this acid to prove their acquaintance with it; but the first person who explicitly described its distinctive characters was Gerard Dornæus, in a work published in the year 1570.

The original process by which this acid was prepared consisted in the distillation of dried copperas, which is the sulphate of the protoxide of iron, called, for brevity, sulphate or protosulphate of iron. As the highly concentrated liquid collected in the receiver had much the appearance of an oil, it received the inappropriate designation of *oil of vitriol*, a name still retained for convenience to signify the concentrated acid. In commercial language it is commonly designated *vitriol*. In Great Britain, France, and most other countries, the process of making sulphuric acid from green vitriol has been abandoned, except when the acid is required for a few particular applications; but it is still practised on an extensive scale at Bleyl, a village in Bohemia, and at Nordhausen in Saxony.*

The chemical changes which take place in the distillation of copperas are the following. The preliminary calcination at a red heat reduces the amount of water of crystallization in the copperas from seven

* The following is an outline of the mode of conducting the distillation of green vitriol, as practised at Bleyl. A detailed account of it may be found in the 51st vol. of the *Journal de Physique*. The retorts employed in the process are pear-shaped earthen vessels, the necks of which are slightly curved to enable them to be adapted to stone-ware receivers. A series of these retorts being arranged in a long horizontal furnace or gallery of brick-work, each retort is charged with three pounds of calcined copperas, and the fire is lighted. On the first impression of heat a small quantity of acidulated water distils over, proceeding from the hygrometric moisture of the copperas; this is allowed to escape, and when no more is observed to come over, the receivers, each containing a

equivalents (the quantity contained in the crystallized salt), to considerably less than a single equivalent. Partly on account of the small proportion of water present, the first portions of sulphuric acid which are expelled from the copperas are decomposed into sulphurous acid gas and oxygen; the former escapes through the luting, and the latter unites with the protoxide of iron (FeO) to convert it into the peroxide (Fe_2O_3). Thus the reddish-brown residue in the retorts at the close of the distillation is peroxide of iron, although the sulphate originally contained the protoxide only. When the iron is fully peroxidized, sulphuric acid passes over and condenses into a fuming dark brown liquid, having a density of about 1.9, which is greater than that of the acid prepared by any of the ordinary processes. Its boiling point is so low as 120° Fahr.

The colour of the acid thus obtained is probably due to an accidental impurity. This acid is generally known by the name of Nordhausen oil of vitriol, from being still prepared at Nordhausen in great quantity. The strongest acid obtained by this process is composed of

Two equivalents of anhydrous sulphuric acid	80
One equivalent of water	9
	<hr/> 89

The fuming of the Nordhausen acid on exposure to the air proceeds from the escape of the anhydrous

little water, are luted to the retorts, and the heat is raised and maintained pretty high for thirty-two hours. The acid rises in the form of a dense white vapour, which is quickly absorbed by the water in the receivers. As the condensation of the vapour develops a considerable degree of heat, the workmen have the means of determining when the distillation is complete by the cooling of the receivers, although the re-

acid in vapour, and the condensation of the moisture in the atmosphere by the acid.

On redistilling the Nordhausen acid at a gentle heat in a glass retort, the receiver being artificially cooled, the anhydrous sulphuric acid, which is extremely volatile, distils over and condenses in the solid state, forming soft, silky, tough crystals, much resembling asbestos in appearance. At 77° Fahr. it liquefies, and at a little higher temperature enters into ebullition, forming a colourless vapour, provided no water is present; but when exposed to the air, it produces dense white fumes by condensing the atmospheric moisture. At 68° Fahr. its density is 1.98. The affinity of the anhydrous acid for water is very intense; if dropped into that liquid in small quantities, it produces a hissing noise, as a piece of red-hot metal, and in larger quantities it produces such a sudden burst of vapour as amounts to an explosion. It contains 1 eq. of sulphur (16), and 3 eqs. of oxygen (24). Its equivalent is therefore 40.

But to return to the manufacture of the acid. The length of time necessary for the operation, the smallness of the product, and the rapid destruction of the retorts through the intense heat requisite, rendered the old process, by means of copperas, extremely tedious and inconvenient. Towards the end of the seventeenth century, the discovery of a more advantageous method was made the object of experiment, and was

retorts are still at their proper heat. When the receivers are become cool, they are disconnected from the retorts, the red oxide of iron remaining in the retorts as the residue of the copperas, is taken out, and its place is supplied with a fresh charge of copperas, and the distillation is recommenced as before. Unless the product of the first distillation is removed from the receivers, it is unnecessary to add more water.

fortunately attained by two French chemists, Lefevre and Lemery. Long antecedent to this, however, it had been observed that a small quantity of sulphuric acid is produced when sulphur is burned in a humid vessel, and some pharmaciens had actually followed this as a manufacturing process; the acid thus prepared was known as *oil* or *spirit of sulphur by the bell*, the name having reference to the glass globe in which the combustion was effected. The grand improvement introduced by Lefevre and Lemery consisted in the addition of nitre to the sulphur in this operation; whereby the product of sulphuric acid is prodigiously increased. For a long time, however, the quantity of sulphuric acid made by this improved process was inconsiderable, and Lemery himself observed that he preferred the acid made without nitre.

The process of the French chemists was first conducted on an extensive scale in England, where Dr. Ward, of Richmond, the inventor of many celebrated nostrums bearing his name, was granted by patent the exclusive right of working the process. The price of the article prepared by Ward was from 1s. 6d. to 2s. 6d. per lb. The glass globes employed in the process were of the capacity of forty or fifty gallons. The mixture of sulphur and nitre was set on fire in an iron ladle, placed on a stone-ware support, a few pounds of water having been previously introduced into the globe. On the expiration of Ward's patent right, several other individuals became concerned in the manufacture, and introduced various improvements, by far the most important of which consisted in the substitution of large leaden chambers for the fragile and expensive glass globes. The first leaden cham-

ber for the purpose was erected at Birmingham, by Dr. Roebuck and Mr. Samuel Garbett, about the year 1746.*

The general manner of conducting the process until within the last eighteen or twenty years was the following. The floor of the chamber being covered with water, a mixture of seven or eight parts of brimstone, with one pound of crude nitre, was spread on leaden or iron plates, supported by stands of lead about a foot above the surface of the water, and the mixture was ignited by a red-hot iron rod. About thirty pounds of the mixture was reckoned a proper charge for a chamber of the capacity of nine thousand cubic feet. Three hours after the sulphur was lighted, the doors of the chamber were thrown open for a quarter of an hour or half an hour, to ad-

* The history of the progress of the manufacture of sulphuric acid has been minutely traced by Mr. Parkes, in his Essay on Sulphuric Acid, to which work I am chiefly indebted for the following particulars. The consumption of the sulphuric acid made by Dr. Roebuck and Mr. Garbett being confined almost entirely to Birmingham and its immediate vicinity, owing to the interior locality of the town, and the risk and expense, at that time, of land carriage, the adventurers were induced, in 1749, to establish works on a very extensive scale at Preston Pans, on the eastern coast of Scotland, expecting that many important applications of the acid would result from affording facilities for its transportation. At Birmingham its chief uses were in the preparation of nitric acid by means of nitre, for the use of the various manufactories, and for recovering the silver and gold of waste plated and gilt metal. A set of experiments on the use of sulphuric acid in bleaching was undertaken about this time by Dr. Home, Professor of Chemistry in the University of Edinburgh, which shewed its decided superiority over sour milk (till then the only acidulous liquid employed in bleaching), and in a short time nearly all the linen bleachers of Scotland and Ireland adopted this acid to the entire exclusion of sour milk.

Until about the year 1756, Messrs. Roebuck and Garbett carried on the manufacture with great success and without any opposition; but one of their workmen at Birmingham, who had absconded from their service,

mit air, and allow the incondensable gases and vapours to escape, preparatory to the introduction of another charge. The chamber was charged in this way six times in the course of twenty-four hours. As soon as the liquid in the chamber attained a specific gravity of 1.350, it was withdrawn by a siphon into a reservoir of lead, and pumped from thence into a leaden boiler: the floor of the chamber was again covered with water. The acid was concentrated in the leaden boiler until of a specific gravity near 1.700, when it was transferred to glass retorts, and then boiled until it attained the strength required.

Since sulphuric acid was prepared in the mode just described, some important improvements have been introduced; but without detailing each of these in

contrived about that time to induce a party at Bridgenorth to establish a manufactory there; and another of their workmen, discharged from Preston Pans, became the founder of the extensive works at Bewdley in Worcestershire. The size of the chambers at Bewdley was ten feet square.

The first manufactory of sulphuric acid in vessels of lead near London was that established at Battersea in the year 1742, by Messrs. Kingscote and Walker, druggists. The scale on which these works were established was very considerable, but in a few years the speculation proved a failure and the manufacture was discontinued.

A very extensive vitriol work was erected about the year 1783, near Eccles in Lancashire, and shortly afterwards another at Leeds. Since the introduction of the method of bleaching by chlorine, and the process of preparing soda by means of common salt, the demand for this acid has been almost unlimited, and the manufacture has gradually extended over almost every part of the United Kingdom. The usual dimensions of the chambers about twenty years ago were, from twenty feet long and twelve feet wide, to forty or sixty feet long and sixteen or eighteen feet wide. At present, chambers are sometimes constructed of one hundred and twenty feet in length, forty feet in width, and twenty feet in height. Other interesting historical particulars relating to the progress of the manufacture of this important acid may be found in the *Chemical Essays* of Mr. Parkes.

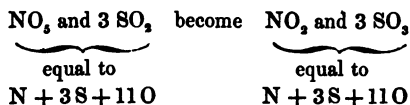
the order of their introduction, we may proceed to describe the methods now most generally practised in this country, neglecting the trifling variations in the minute details of the manufacture, which may be met with in different works. It will be convenient, however, first to consider the nature of that reaction between the sulphur, nitre, air, and water, which is the foundation of this important process.

It was formerly considered that the formation of sulphuric acid in the ordinary process, is *solely* a consequence of the direct oxidation of sulphurous acid formed by the combustion of sulphur in the air, by the oxygen contained in the nitre. The latter, it is well known, has a great oxidizing power; as a consequence of its containing nitric acid (NO_3), which easily parts with its oxygen; without reference, therefore, to the relative weights of nitre and sulphur employed, and of sulphuric acid produced, this would seem to be a correct explanation of the change which occurs. But a very simple calculation suffices to prove the fallacy of such a view. If we consider the relative *weights* of the materials and of the product, and it is only by observing the weights of the acting bodies that we obtain proper data for the foundation of a theory of any chemical reaction, it will be perceived that the quantity of nitre sufficient for a successful operation does not contain enough oxygen to convert one-twentieth part of the sulphurous acid into sulphuric acid. Where then is the source of oxygen? It cannot be *water*, for the whole of that liquid employed in the process is found at the end, unaltered, except in being in combination with sulphuric acid. The only remaining source of oxy-

gen is the *atmosphere*; and it has been amply demonstrated, that, with the exception of a trifling quantity derived from the nitre, the whole of the oxygen required is obtained from the air; although when sulphur is burned in dry air, not a particle of sulphuric acid is produced, and in moist air, over a surface of water, the quantity formed is but a mere trace. The complicated changes by which the sulphuric acid is produced have been most clearly traced; and though there are still a few trifling points connected with it which remain undecided, yet few chemical reactions taking place among four different bodies, as in the present instance, admit of a more satisfactory explanation.

The acting substances are,—1°, sulphurous acid (SO_2), formed by the combustion of sulphur in the air; 2°, nitre or nitrate of potash, the nitric acid (NO_3) of which only comes into play; 3°, the air, composed of very nearly one volume of oxygen and four volumes of nitrogen; and 4°, water or steam.

At the very commencement of the process a reaction takes place between the sulphurous acid and nitric acid, different from those changes by which the greater part of the sulphuric is formed, consisting in the conversion of nitric acid to nitric oxide (NO) by the transference of three equivalents of oxygen to three equivalents of sulphurous acid, with formation of three equivalents of sulphuric acid: thus



The sulphuric acid thus produced is condensed by

the water on the floor of the chamber, and is retained there; but the nitric oxide, which is a gaseous body, invisible when pure, becomes diffused into the atmosphere of the chamber to perform a most important part in the subsequent reactions. Nitric oxide possesses the remarkable property of instantly uniting with more oxygen whenever presented to that gas, or to a mixture containing it in the free state, as the atmosphere itself. If the oxygen is present in sufficient quantity, a compound is formed consisting of one equivalent of nitrogen and four equivalents of oxygen, to which the name *peroxide of nitrogen* is applied; but if the quantity of oxygen is insufficient for the formation of that substance, a compound is produced containing one equivalent of nitrogen and three equivalents of oxygen, known by the name of *nitrous acid*.* This property of nitric oxide to abstract oxygen from the air is of the highest importance in the changes which take place in the leaden chamber.

The atmosphere of the chamber, which is the scene of action, contains therefore

Sulphurous acid,
Peroxide of nitrogen,
Air, and
Steam.

The next point which demands consideration is the action which sulphurous acid and peroxide of nitrogen exert on each other.

* On introducing copper filings into nitric acid of moderate strength, nitric oxide gas is evolved. When pure, this gas is colourless, but immediately it comes into contact with the air, a reddish-brown vapour is perceived, owing to the formation of either nitrous acid (NO_2), or peroxide of nitrogen (NO_4), according to the proportion of air or oxygen which may be present.

If these bodies are mixed perfectly *dry* in the state of *gas*, no change whatever, neither combination nor decomposition of any kind occurs. But if a little steam is admitted to the mixture of the two gases, combination ensues, and a white solid in small feathery crystals is produced. The presence of a little sulphuric acid already formed greatly facilitates the combination. These crystals contain the elements of one equivalent of nitric acid and two equivalents of sulphurous acid, but the precise mode of arrangement of the elements is uncertain; for our purpose it may be conveniently considered as a compound of sulphurous acid and peroxide of nitrogen together with sulphuric acid, according to the formula $(\text{SO}_2 + \text{NO}_2) + \text{SO}_3$.

This crystalline compound, it is to be observed, is formed only when a small quantity of water is present. On coming into contact with more water, it is instantly decomposed, with the formation of sulphuric acid on the one hand and nitrous acid on the other. This change is effected through the transference of one equivalent of oxygen from the peroxide of nitrogen to the sulphurous acid; the crystalline substance producing, according to the formula given above, two equivalents of sulphuric acid and one equivalent of nitrous acid; thus, $(\text{SO}_2 + \text{NO}_2) + \text{SO}_3$ and 2 eqs. of HO , become NO_2 and $2 (\text{SO}_3 + \text{HO})$.

Of these products, the sulphuric acid is immediately precipitated on the walls and floor of the chamber, but the nitrous acid spontaneously decomposes into nitric oxide and peroxide of nitrogen; one equivalent of each of these gases being produced through the de-

composition of two equivalents of nitrous acid; thus, 2NO_2 (or $\text{N}_2 + \text{O}_6$) = NO_2 and NO_4 .

But no sooner is nitric oxide thus reproduced, than it unites with more oxygen of the air (provided sufficient be present), and once more changes to peroxide of nitrogen. The peroxide thus reproduced on meeting a second time with sulphurous acid and water gives rise to a succession of the same changes, with the formation of an additional quantity of sulphuric acid and reproduction of peroxide of nitrogen and nitric oxide; and the latter, by uniting with oxygen, again becomes peroxide of nitrogen. These changes continue so long as the necessary sulphurous acid, water, and air are supplied.

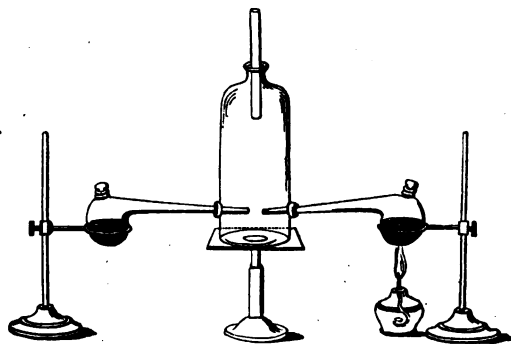
It appears, therefore, that the source of oxygen necessary to convert the sulphurous acid into sulphuric acid, is neither peroxide of nitrogen nor nitric oxide, primarily, but the air, the nitric oxide merely acting as the means of transferring the oxygen. The changes are in reality simple, though the several incidental circumstances occurring at the same time somewhat complicate its description. Nitric oxide takes oxygen from the air and then transfers it to sulphurous acid, becoming again fitted to abstract oxygen from the air and continue the action. On this principle only, for the enunciation of which we are indebted to MM. Clement and Desormes and Sir Humphrey Davy (though the original theory has met with some slight modifications), can the fact be accounted for that a comparatively trifling quantity of nitre is sufficient to convert a large quantity of sulphur into sulphuric acid.

The reason why an indefinite quantity of sulphur cannot be converted into sulphuric acid through the agency of the same quantity of nitric oxide (as would seem to be required by the above view) is evidently because the nitric oxide is removed from the chamber by being mixed with the nitrogen of the air, the oxygen of which has been completely abstracted. If the chamber could be supplied with pure oxygen gas and pure sulphurous acid, a very small quantity of nitric oxide might suffice for the production of an unlimited quantity of sulphuric acid.

The formation of sulphuric acid in this way admits of some instructive illustrations on the small scale. If a little sulphurous acid gas is introduced into a bottle, the sides of which have previously been wetted with some concentrated nitric acid, the bottle becomes beautifully coated with the white crystalline compound. The flask belonging to the apparatus figured at page 355 may be used in this experiment, the exit-tube being simply dipped into the bottle. Either charcoal and oil of vitriol, or metallic copper and oil of vitriol, may be used as the source of the sulphurous acid gas. If the nitric acid employed in this experiment is very strong, the crystals formed will be tolerably stable. On introducing a little water, their immediate decomposition takes place, with effervescence of nitric oxide and peroxide of nitrogen, while sulphuric acid remains dissolved in the water.

A more exact imitation of the process may be performed by means of the apparatus represented in the annexed figure. It consists of a tall glass jar, having three openings, two near the bottom and one at top.

Fig. 36.



Through the opening at top is inserted a glass tube open at both ends. With the two lower openings are connected two stoppered retorts, one of which contains some slips of copper, and the other materials for evolving sulphurous acid. Before the apparatus is arranged, the sides of the bottle should be wetted all over with oil of vitriol, and a few drams of that liquid may be allowed to remain at the bottom. Heat is first applied to the retort for evolving sulphurous acid; and when that gas begins to be evolved with tolerable rapidity, but before much has entered the bottle, nitric acid of about the specific gravity 1.2 is poured on the copper in the other retort to evolve nitric oxide gas. Should the production of the gases become so violent as to expel too much of the air of the bottle, the stoppers of the retorts may be withdrawn and the gases allowed to escape for a little while. The crystalline compound soon forms a beautiful coating on the sides of the bottle. On introducing more water it is rapidly decomposed, and peroxide of nitrogen is

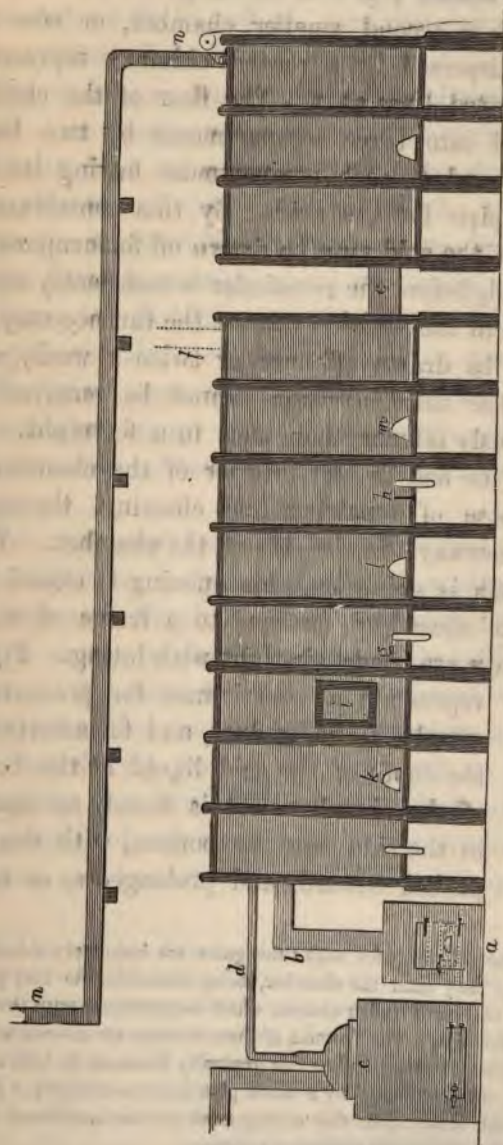
reproduced to act on another quantity of sulphurous acid.

But to return to the process practised on the large scale. Of late years, iron pyrites has been very extensively used in the manufacture of oil of vitriol; but as sulphur is not yet wholly superseded by pyrites, the following account has reference, in the first place, to the use of sulphur only. A sulphuric acid chamber, with most of its appendages, is represented on the opposite page. It is supported on brick or stone pillars, and by an external wooden frame-work at seven or eight feet above the ground level.*

The sheet-lead of which the bottom of the chamber is made should weigh eight or ten pounds to the square foot; but for the top and sides, lead of one half that thickness is sufficient. The combustion of the sulphur with nitre is effected in the small furnace *a*; it is generally built entirely of fire-brick, but the roof and floor are sometimes formed of cast-iron plates. The quantity of air which enters is regulated by a damper attached to the door. The sulphurous acid gas produced through the combustion of the sulphur, air, and gases from the nitre are conducted from the furnace *a* by means of an iron pipe *b*, about ten or twelve inches in diameter, into the leaden chamber, where it becomes mixed with steam proceeding from the boiler *c* through the pipe

* By giving the chamber this elevation the acid may be easily conveyed by pipes to the boilers or elsewhere, without the trouble of pumping or transferring into bottles: access is readily obtained to the bottom of the chamber for repairing, and the room below may be made available for other purposes.

Fig. 37.



*d.** At the bottom of the other end of the chamber is a large leaden pipe *e* to discharge the uncondensed gases into a second smaller chamber, or else they may be dispersed by a second chimney represented by the dotted lines at *f*. The floor of the chamber is divided into three compartments by two leaden ridges, *g* and *h*, each compartment having its proper exit-pipe for the acid. By this contrivance a portion of the acid may be drawn off for evaporation, if required, before the remainder is sufficiently strong. The acid in the division nearest the furnace may, for instance, be drawn off once or twice a week, while that in the third division cannot be removed advantageously oftener than once in a fortnight. Access may be had to the interior of the chamber for the purpose of repairing and cleaning, through a hole or doorway *i* in the side of the chamber. While the process is going on, this opening is closed with a piece of sheet-lead fastened to a frame of wood; the joinings are made air-tight with luting. Fig. 38

Fig. 38. represents a contrivance for procuring a sample of the product, and for ascertaining the depth of the acid liquid at the bottom of the chamber. It is merely an opening in the side near the bottom, with the lead pushed inwards and prolonged so as to dip



* In some oil of vitriol works the gases are intimately mixed with steam before they enter the chamber, being introduced for that purpose into one or two small leaden cisterns which communicate with the chamber by a large pipe. The bottoms of these cisterns are covered with two or three inches of water, and as this gradually increases in bulk and becomes acid, it is conducted by a waste pipe into the chamber. But the benefits which result from this arrangement are not considered by any means proportional to the additional expense.

beneath the surface of the liquid, and thus prevent the escape of gas. In fig. 37 three such openings are represented at *k*, *l*, and *m*, one pertaining to each compartment of the floor.

The chambers of some oil of vitriol works are divided into rectangular compartments by parallel leaden curtains, of which there may be three or four in a chamber of eighty feet in length; these reach across the whole width of the chambers, but not from top to bottom, wanting about six inches, the opening being left at top and bottom alternately, so that the gaseous mixture having entered a compartment at the top of one screen passes out at the bottom of the next, and so on. The object of this arrangement is to occasion a more complete intermixture of the gases.

The apparatus being properly arranged, the floor of the chamber is first covered with a stratum of a few inches in depth of dilute sulphuric acid; the acid is employed for this purpose in preference to water, as it causes the action to proceed with more vivacity.* The sulphur is then placed in its burner, and immediately over it is supported an iron pot containing the nitre or nitrate of soda,† mixed with the quantity of sulphuric acid proper for its decomposition. A hundredweight of bruised brimstone re-

* The presence of sulphuric acid considerably facilitates the union of sulphurous acid and peroxide of nitrogen, because it enters as an essential constituent into the composition of the crystalline compound (see p. 370).

† Either common nitre or nitrate of soda may be used indifferently, these salts being equally effective. In his choice, the manufacturer is guided by the respective prices of the articles, and by his facilities for disposing of the sulphates which remain after the decomposition. When common nitre is used, the residue consists of sulphate of potash, for

quires from eight to ten pounds of nitre, or else from seven to nine pounds of nitrate of soda, and from five to six pounds of oil of vitriol. In some works the nitre or nitrate of soda and oil of vitriol are mixed with the sulphur, instead of being supported over it. The sulphur being kindled, the heat it produces vaporizes nitric acid; but the latter is immediately reduced by sulphurous acid to the state of nitric oxide, and as such proceeds to the chamber accompanied by sulphurous acid, air, and steam supplied by the boiler. The quantity of sulphur employed is of course proportioned to the size of the chamber. For a chamber of which the capacity is 27,000 cubic feet, nine hundredweight of sulphur may be consumed in the course of twenty-four hours.

The introduction of water into the chamber in the form of steam is one of the most important of the modern improvements in this manufacture, being the principal cause of the larger product and increased rapidity of the present process compared with the old method. Water or steam not only performs an essential chemical action, but steam operates mechanically in causing the gaseous molecules to mix intimately and bring them more nearly into a state of juxtaposition; and it also quickens the chemical changes by the heat it affords. The amount of steam

which there is a considerable demand at the alum works in the North of England. The residue from nitrate of soda, which is sulphate of soda or *salt-cake*, is inferior in value to sulphate of potash, but meets with a purchaser in the soda manufacturer. In a few sulphuric acid manufactories, where a considerable quantity of nitric acid is regularly consumed in the preparation of oxalic acid and certain metallic compounds, the nitrous vapours which are thus evolved are made available as a substitute for nitre, being simply conducted into the leaden chamber.

introduced is regulated by the condition of the chamber. If a small quantity of the gaseous mixture, allowed to escape from the chamber through an opening in the side, smells but feebly of sulphurous acid, the steam should be diminished and the combustion of the sulphur facilitated by stirring and admitting more air. But if the odour of sulphurous acid is stronger than it ought to be (a point easily decided by an experienced workman), the proportion of steam should be increased. The state of the chamber may also be ascertained by collecting and examining a little of the acid as it trickles down the sides of the chamber. For that purpose a small ledge is fixed as a receiver for the acid to the inside of the chamber, from which the acid may be withdrawn on the outside at pleasure by a small leaden pipe. If it evolves much nitrous fumes when mixed with water, the proportion of steam may be increased, and that of nitre diminished. But if it develops no nitrous vapours when mixed with water, and possesses a strong odour of sulphurous acid, the proportion of nitre should be increased.*

It has already been observed (page 370) that the existence of the crystalline compound is exceedingly transitory, it being decomposed almost immediately on its formation, when the action proceeds in a proper manner. But when the proportion of water present is small, and especially if the temperature

* The state of the interior of the chamber may also be ascertained by having two or three circular openings in the roof of the chamber, each of which is covered with a glass bell-jar fitting into a groove around the opening. Whenever the interior of the jar does not appear thickly covered with drops, the proportion of steam in the chamber should be increased.

happens to be low, the crystals are sometimes precipitated and remain for a considerable time without decomposition, forming a crust of half an inch or more in thickness on the sides of the chamber. As the atmosphere of the chamber is thus deprived of its nitric oxide or peroxide of nitrogen, unless the temperature is raised or more steam introduced to cause the decomposition, the formation of more sulphuric acid is prevented.* A convenient temperature at which to maintain the chamber is 130° or 140° Fahr.

On considering the chemical changes which occur in this process, it will be manifest that if the supply of sulphurous acid and air is properly apportioned, the only refuse is the nitrogen gas of the air, together with some nitric oxide gas, means for the exit of which should be provided by a waste-pipe. In fig. 37, this part of the apparatus is represented at *n*. The pipe may be prolonged to eighty or a hundred feet to ensure the complete condensation of the acid. Nitrogen being a comparatively light gas is displaced by the influx of heavier gases at *e*.

Iron pyrites was first extensively employed in the manufacture of sulphuric acid by Mr. Hill, proprietor

* The influence of temperature on the reactions which take place in the leaden chamber has been demonstrated in a decisive manner by an experiment of MM. Clement and Desormes. Into a glass globe containing a small piece of ice they introduced simultaneously sulphurous acid, oxygen, and nitric oxide, and plunged the globe in ice-cold water. The consequence was, that no sulphuric acid was formed, though all the materials necessary to its production were present; but on heating the globe to the temperature of 100° Fahr., immediate action ensued, and hydrated sulphuric acid was condensed on the sides of the globe in visible stræ.

of chemical works at Deptford and at Battersea, who obtained a patent for the application of this and other native sulphurets in 1818. Since the expiration of Mr. Hill's patent right, and especially since the attempt to establish a monopoly in the sulphur trade, many other manufacturers have availed themselves of this material, so that, at present, pyrites is much more largely employed than sulphur. When this mineral is calcined in such a manner as to have free access of air, the whole of its sulphur burns off as sulphurous acid, leaving a residue of red oxide of iron.

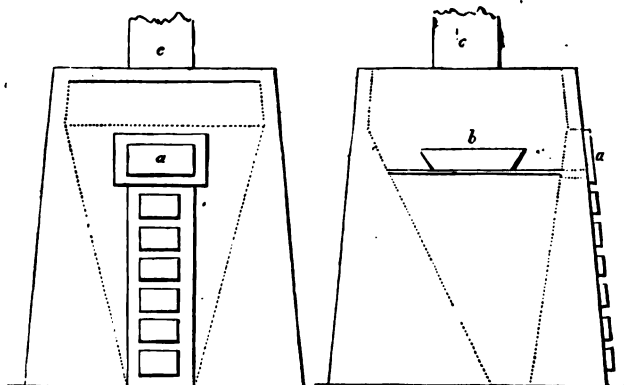
The presence of arsenic in larger or smaller proportions in all the ordinary varieties of this mineral constitutes one capital objection to its application in the manufacture of sulphuric acid, the acid it affords being always slightly contaminated with arsenic (arsenious acid). The quantity of this substance, however, which finds access to the chamber is seldom more than a mere trace, for nearly the whole is condensed in the flue of the pyrites burner; the flue being prolonged, in some works, to the length of thirty or forty feet, to expose it to the cooling influence of the atmosphere. The pyrites met with at the Isle of Sheppy is almost entirely free from arsenic.*

The construction of the ordinary pyrites burner

* In the specification of a patent for some improvements in the manufacture of sulphuric acid (obtained in 1840), Messrs. Blair and Watson claim the use of sulphuretted hydrogen as a means of separating arsenic from sulphuric acid. The acid is submitted to the action of sulphuretted hydrogen in the state in which it is withdrawn from the chamber, when the arsenic is precipitated from the dilute acid in the state of orpiment, or King's yellow. Sulphuretted hydrogen occasions no precipitate unless the acid is dilute.

Fig. 39.

Fig. 40.



may be conceived by reference to figs. 39 and 40. Fig. 39 represents the front, and fig. 40 a perpendicular section from the front to the back. The burner somewhat resembles a lime-kiln, its interior space being in the form of an inverted pyramid. Its entire height from the basement is from eight to ten feet; its external width at bottom from seven to nine feet, and at top about six or seven feet. Its widest part in the interior is at seven or eight feet from the base, where the width is five or six feet; from this it contracts gradually to the bottom, where it is about two feet wide. The mineral is broken into small pieces about the size of a hen's egg, and thrown into the burner through the top or feeding door *a*. Across the interior, on a level with this door, are placed a few iron bars to support the nitre pot *b*, fig. 40. From the bottom of the burner to the door *a* are five or six smaller doors for stoking the ore in its descent. All the doors except the lowest are made tight with luting during the combustion of the

pyrites, the air having access through the bottom door only. The gases are conducted from the burners by the flue *c*, and the calcined ore is withdrawn at the bottom door. In a burner of this construction, and of the largest size above mentioned, about a ton of pyrites may be burned in twelve hours, the ore being introduced every hour.

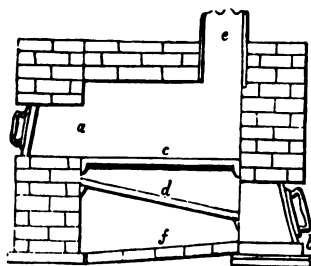
In the form of small masses pyrites is sufficiently combustible to continue burning of itself, when once ignited with a proper supply of air; but if finely divided, its combustion generally requires to be assisted by heat derived from another source. One form of burner for small pyrites comprises two rectangular earthenware retorts, each about ten feet long, three feet deep, and two feet broad, with an earthen shelf extending its whole length, placed horizontally. The retorts are supported by several rows of fire-brick. Between the two retorts is the fire-place, about two feet in width and five feet in length; the fire plays around each retort, passing through the spaces between the rows of bricks which support the retorts. Air enters the retort through a small aperture in the door at one end, and the gases pass out at the other end and are conveyed into the flue of the large burner. About a ton and a half of small pyrites may be burned in the two retorts in twenty-four hours.*

A patent has been lately obtained by Mr. Farmer for a furnace of particular construction for the com-

* The burner for small pyrites at some works consists of a series of several shelves of fire-tiles placed at four or five inches apart. The breadth of the burner is about six feet; its height three feet six inches, and its depth eight feet. Each shelf is furnished with openings through the iron door in front, to introduce the pyrites and withdraw the calcined ore. The shelves do not reach quite to the back

bustion of pyrites and other sulphurets, with a view of obtaining either sulphurous acid or sulphur without the aid of fuel. A perpendicular section of the furnace is represented in fig. 41. The furnace is first heated with coals or burning pyrites from a previous operation, and then fed with pyrites in small lumps through the door-way *a*; the amount of air

Fig. 41.



necessary for the combustion is regulated by that opening, and also by the doorway *b* on the other side at bottom. The small fragments which fall through the grate *c* are received in a second grating *d*, the bars of which are placed closer together

than those of *c*. The sulphurous acid gas produced by the combustion of the pyrites escapes by the chimney *e*, and is conducted into the leaden chamber. To obtain sulphur from pyrites by this furnace, the doorway *a* is kept entirely closed except when more pyrites is to be introduced, just sufficient air being admitted through the opening *b* to maintain the pyrites in a state of low combustion. A little unburned sulphur is then given off, and may be collected in a leaden chamber or receiver communicating with the furnace by the chimney *e*. The occasional admission

of the burner, so that a clear space exists there through which the sulphurous acid from all the shelves rises and escapes at the flue. The nitre pot is introduced through an opening at the back of the burner, and the extraneous heat necessary to assist the combustion of the small pyrites is derived from a furnace situated on one side of the burner.

of steam obtained by throwing water on the ash-hole *f* is said to facilitate the extrication of the sulphur.*

The small pyrites may be advantageously consumed in a burner constructed in the ordinary manner (as figs. 39, 40), if previously worked up into small bricks with about one-fourth of its weight of plastic clay.

Most of the pyrites used in the English sulphuric acid manufactories, with the exception of those near London, is procured from Ireland, particularly from the county of Wicklow. An abundance may be obtained from Cornwall; but the pyrites raised in that county usually contains a much larger proportion of arsenic than that found in Ireland. The cost of this mineral must of course vary exceedingly with the locality of the works. The best pyrites is delivered at Runcorn (the port of most of the Lancashire works), at about 1*l.* 7*s.* per ton. A ton of pyrites requires about sixty pounds of nitre, with the equivalent quantity of sulphuric acid, and if good, affords nearly a ton of the concentrated acid.

Attempts have been made at different times in the manufacture to apply of sulphuric acid the sulphurous acid produced by the combustion of sulphuretted hydrogen; the latter being an abundant bye-product in a few manufacturing processes, particularly in the production of ammoniacal salts from gas liquor. In a process of this kind, included in a

* The decomposition of iron pyrites by steam, at a high temperature, with formation of sulphuretted hydrogen gas and oxide of iron, has been made the basis of a process for effecting the complete separation of sulphur from pyrites, for which a patent has been granted to Mr. Julian Rodgers of Pimlico.

patent granted to Mr. Maugham in 1836,* the sulphuretted hydrogen is mixed, in a row of little separate boxes contained in an air-tight iron vessel, with the quantity of atmospheric air or oxygen gas proper for its complete combustion, the gases being contained in two gas-holders. The mixture burns at small jets proceeding from the boxes, and the sulphurous acid and steam produced by the combustion are conducted by a pipe from the external iron vessel into the leaden chamber, where it is oxidized through the agency of nitric oxide in the usual way. The jets are lighted at first through an opening in the exterior vessel, which is afterwards closed and rendered air-tight.

When the sulphur monopoly was in force, an attempt was also made to apply for the same purpose a compound of lime and sulphuret of calcium, obtained as a bye-product in the process of making carbonate of soda from common salt. This compound is technically known as *soda-waste*. Hydrochloric acid, another bye-product of the same process, which is commonly allowed to escape by the chimney, is collected and applied to the soda-waste; the latter being in a humid state. Sulphuretted hydrogen and carbonic acid gases are immediately disengaged, and the former may be burned instead of sulphur to produce sulphurous acid. But the quantity of hydrochloric acid which may be collected in the soda process is not sufficient to decompose the whole of the soda-waste; the decomposition of the remainder, however, may be effected by means of the carbonic acid disengaged

* For "certain improvements in the production of chloride of lime and certain other chemical substances."

with the sulphuretted hydrogen, which forms carbonate of lime and an additional quantity of sulphuretted hydrogen. This process was devised by Mr. Gossage.*

Mr. Peregrine Phillips has contrived a process for preparing sulphuric acid on the large scale without the aid of nitre, founded on the property possessed by spongy platinum of causing chemical combination between certain gases with which it is placed in contact, as hydrogen and oxygen, hydrogen and chlorine, and sulphurous acid and oxygen. When a mixture of sulphurous acid and air is made to pass over

* Gypsum, or sulphate of lime, of which a great abundance might be procured, has been recently proposed as another source of sulphur, by M. Thaulow. It is proposed that the sulphate of lime be first reduced to the state of sulphuret of calcium by calcination with charcoal in iron or earthen retorts. In this operation the carbon unites with the whole of the oxygen of the sulphate of lime, forming carbonic acid (according to M. Thaulow), which comes off in the state of gas, the remaining constituents of sulphate of lime forming sulphuret of calcium. The carbonic acid gas is not suffered to escape, but is employed for the decomposition of sulphuret of calcium obtained by a previous operation well mixed with water. By the action of carbonic acid on sulphuret of calcium in the presence of water sulphuretted hydrogen gas is disengaged, carbonate of lime remaining as the residue. The evolved sulphuretted hydrogen gas is conducted immediately into the leaden chamber and there burned, when it gives rise to water and sulphurous acid: the latter is to be oxidized by the agency of nitric oxide in the usual manner.

The preceding process has not yet, I believe, been introduced on the large scale. Its success, in its present form, depends partly on the circumstance that sufficient carbonic acid is generated by the action of charcoal on a given quantity of sulphate of lime, to decompose the sulphuret of calcium produced by the same quantity of sulphate of lime in a previous operation. For carbon to effect the complete decomposition of the sulphate with formation of nothing besides carbonic acid and sulphuret of calcium, one equivalent of sulphate of lime requires exactly two equivalents of carbon; thus, CaO, SO_3 and $2\text{C} = \text{CaS}$ and 2CO_2 . But with only two equivalents of carbon to one of the sulphate, the decomposition goes on slowly, requires a high temperature, and is probably never com-

spongy platinum heated to redness, combination ensues between the sulphurous acid and the oxygen of the air with formation of sulphuric acid. In the process of Mr. Phillips, sulphurous acid is mixed with an excess of air by a blower, and caused to pass through a red-hot platinum or porcelain tube, filled with spongy platinum or balls of fine platinum wire. The vapours of sulphuric acid thus generated, which are mixed with the nitrogen of the air, and the excess of air, are conducted by a tube of lead into a long and narrow leaden condenser, supported in an upright position by masonry. The condenser is filled with quartz pebbles, which are kept constantly wet with a stream of

plete. With an excess of carbon it is effected readily and completely; but in that case, instead of carbonic acid, a certain amount of carbonic oxide is evolved, which does not possess the power of decomposing moist sulphuret of calcium like carbonic acid. Again, in most countries the only substance which could be economically employed in the reduction of sulphate of lime to the state of sulphuret of calcium, is coal, the hydrogen of which plays as important a part in the reduction as the carbon; water being formed by the combination of hydrogen with the oxygen in the sulphate, to the diminution of the proportion of carbonic acid and carbonic oxide. Here are material objections to M. Thaulow's process in its present form: but a supply of carbonic acid sufficient for the decomposition of the sulphuret of calcium may be easily obtained from another source; for instance, from the combustion of coke in the furnace in which the vessels containing the mixture of sulphate of lime and carbon are heated. Or, by employing such an excess of carbon in the decomposition of the sulphate of lime that very little or no carbonic acid is given off, the carbonic oxide may be set on fire (air having access), and the carbonic acid thus generated made available in the process. Instead of burning the sulphuretted hydrogen within the leaden chamber, as proposed by M. Thaulow, it would, doubtless, be found more convenient to burn it without, and to conduct the products of the combustion together with a proper quantity of air into the chamber by a large tube. But with these modifications it is improbable that the process would present any economical advantages over the ordinary methods; at least, so long as iron pyrites and sulphur continue so accessible as at present.

water or of dilute acid from the bottom of the condenser, admitted at the top. It is to be expected that, after the spongy platinum has been in use for a long time, its particles will have become so aggregated as to lose their property, in a considerable degree, of causing the condensation and union of the gases.

The only operations in this manufacture which remain to be noticed, are those which have for their object the concentration of the acid. For some manufacturing purposes in which acid of the greatest strength is not essential, as for the preparation of bleaching powder, muriatic acid, and sulphate of soda for the alkali manufacturer, the acid may be used as taken from the chamber without further concentration. But if intended for the market, it must be brought to the greatest strength easily attainable; and even for the purposes above mentioned, some manufacturers employ the concentrated acid, because those parts of the apparatus employed which are constructed of iron are not so easily acted upon by that as by a dilute acid.

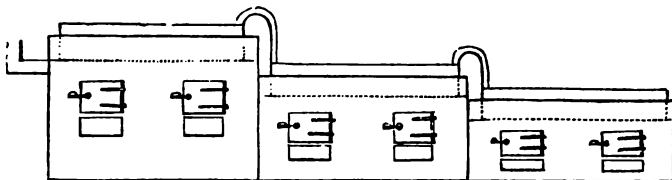
By prolonging the process, acid may be procured from the chamber of a density near 1.500; but when the chamber contains acid of such strength, the action proceeds very tardily, in consequence of the slowness with which such acid decomposes the crystalline compound of peroxide of nitrogen and sulphurous acid, which may remain in solution in the acid even after concentration by evaporation.* For the same

* M. Adolphe Rose has observed, that when acid of specific gravity 1.500, containing the nitrous compound, is distilled, at one period of the distillation, pure sulphuric acid passes over, the proportion of the nitrous compound in the residue thus becoming increased.

reason, acid of greater strength than 1·450 cannot be obtained from the chamber without increasing the proportion of nitre; and even with the increased proportion, the product of acid is small (Mr. Blyth). So that in general it does not answer the manufacturer's purpose to allow the acid to remain in the chamber after it has attained 1·350 or 1·450. If weaker than 1·300, it generally contains in solution a considerable quantity of sulphurous acid.

When of the proper strength, the acid is conveyed by a leaden pipe from the bottom of the chamber to large leaden boilers, in order to be concentrated by evaporation. The boilers are made out of large rectangular leaden plates of twelve or fourteen pounds to the square foot, by folding up the edges so as to make pans of the depth of ten or twelve inches, the corners being turned towards the sides. The annexed figure

Fig. 41.



is a representation of a set of three such boilers, arranged in one line, but at different levels. Each rests on a grate of strong iron bars; and if fuel is not very expensive, has a separate fire. As the acid in the highest boiler becomes concentrated, it may be transferred by a siphon-tube to the middle boiler, and from thence to the lowest; so that the latter always contains the strongest acid. Six evaporating pans,

each presenting a surface of twenty square feet, are sufficient for an establishment where the produce of concentrated acid is from twenty to twenty-four thousand pounds weekly.

But the concentration of the acid cannot be completed in the leaden boilers, from two circumstances : 1°, The boiling point of sulphuric acid of the highest degree of concentration (sp. gr. 1·848) is above the temperature of the melting point of lead ; and 2°, when the density of the acid is greater than 1·75, the lead is corroded, sulphate of lead being formed, to the loss and deterioration of the acid as well as the destruction of the boiler. So soon, therefore, as the acid acquires the density 1·65 or 1·7 in the last leaden boiler, it is cooled, and transferred to glass or platinum retorts to undergo a final concentration to the specific gravity 1·845 or 1·848. In all extensive manufactories, platinum retorts have now entirely superseded those of glass ; a great saving being thereby effected in fuel, breakage, and labour. Notwithstanding the great first cost of a platinum retort or boiler (from one to two thousand pounds), and though their duration is seldom more than three or four years, yet the economy of their employment was manifest, soon after their introduction, by a fall in the price of the acid from fourpence to about three halfpence per pound. The platinum vessel is not exposed immediately to the fire, but is fitted to the inside of a cast-iron pot, to which the fire is applied directly. Towards the end of the concentration, a great deal of sulphuric acid vapour comes over ; which, when glass retorts were employed, was allowed to escape into the atmosphere, to the great annoyance of the surrounding

neighbourhood. These vapours are now conducted into the chamber, where they are condensed; an intolerable nuisance is thus avoided, and a considerable saving of acid effected. Sometimes a leaden condensing worm is attached to the beak of the retort, and the liquid collected by it is returned to the leaden boilers.

When the acid has acquired the proper degree of concentration, it is cooled as speedily as possible, that it may be transferred into carbuys, and the retorts again employed for the same operation. The refrigeration is effected either by letting down the body of the retort into a cistern of cold water, or by running the acid slowly through a platinum siphon, the long limb of which is in the form of a spiral, and surrounded by cold water in a tub. When properly arranged, a platinum retort, capable of holding five and twenty gallons, admits of the concentration of from sixty to seventy gallons of acid (oil of vitriol) in a day.

The average product of concentrated sulphuric acid is about three pounds from one pound of sulphur. By calculation, one pound of pure sulphur should afford just three pounds and one ounce of concentrated acid.

The superiority of the modern continuous process over the old intermittent plan (page 365) must now be obvious. The atmospheric air necessary to the proper action of the chamber was formerly obtained by throwing open several doors four or five times in twenty-four hours, to the loss of about one-third of the sulphurous acid, and to the extreme annoyance of the workmen and the neighbourhood. The requisite vapour was produced by placing several fires within the chamber, which caused an evaporation from the sur-

face of the dilute acid; these fires were lighted and cleared out at each charge of sulphur and nitre, which required a considerable amount of labour, now unnecessary.

When well prepared, concentrated sulphuric acid or oil of vitriol is composed of one equivalent of anhydrous sulphuric acid and one of water, thus :

1 eq. dry sulphuric acid	40	81·63
1 eq. water	9	18·37
	<hr/> 49	<hr/> 100·00

As met with in commerce, its density is 1·847 at 60° Fahr.; but the presence of a little saline impurity contributes to its density in a slight degree. When re-distilled, it is near 1·845. It is a dense, colourless liquid, of an oily consistence, which boils between 610° and 620°, and distils over like water. The temperature at which sulphuric acid boils varies with its strength: when of the specific gravity 1·78, its boiling point is 435° Fahr.; at the specific gravity 1·65, the boiling point is 350° Fahr. At —29° F. the concentrated acid freezes, sometimes assuming the form of regular six-sided prisms of a tabular form. It is so corrosive that a single drop allowed to remain on the skin causes an ulcer; and if a small quantity is swallowed, an intense agony ensues, which speedily terminates in death. Chalk or magnesia mixed with water and syrup is a convenient and efficient antidote.*

* A striking experiment illustrative of the powerful action of the concentrated acid on organic matters consists in mixing about equal bulks of very strong syrup and oil of vitriol. In a few seconds the mixture becomes black and hot, effervesces, and is at last converted into a

Sulphuric acid is the most powerful of acids; it is capable of liberating all others from their saline combinations, with a few exceptions, and these exceptions only under particular circumstances. Its acid property is so strong that it is capable of reddening a blue infusion of litmus when diluted with a hundred thousand times its bulk of pure water. The hot concentrated acid is capable of dissolving a small quantity of sulphur, whereby it acquires a brown tinge; if the mixture is boiled, sulphurous acid is produced. Oil of vitriol dissolves charcoal to a small extent, and thus acquires a reddish colour. If charcoal is heated with the acid, sulphurous acid and carbonic acid gases are given off. The concentrated acid is also decomposed when heated with phosphorus, sulphurous and phosphoric acids being thus produced.

If oil of vitriol is exposed to the air, it rapidly absorbs moisture, and increases in bulk at the same time. In a damp atmosphere, three volumes of the concentrated acid increase to four volumes in the course of twenty-four hours, and a much larger quantity of water may be acquired by a longer exposure. For this reason it is usefully employed in the laboratory, to dry gases, and for evaporation and desiccation *in vacuo*.

The combination of sulphuric acid with water is attended with the developement of a considerable amount of heat. If the bulb of a thermometer is

solid magma of charcoal, or rather of a highly carbonized substance resembling charcoal in appearance. The hydrogen and oxygen of the sugar appear to form water under the influence of the powerful affinity of the sulphuric acid for that compound, the carbon of the sugar being set at liberty. The brown colour which oil of vitriol acquires when exposed to the air is owing to the decomposition of organic bodies which were floating about in the atmosphere.

placed in a vessel of cold water, and concentrated sulphuric acid gradually added, the temperature is seen to increase instantly, and rise to a certain extent. When four parts by weight of the most concentrated acid are suddenly mixed with one part of water, both being at 50° Fahr., the temperature of the mixture rises to 300° (Dr. Ure). Mr. Parkes states, however, that the highest temperature he was able to procure was 266° Fahr., which was obtained by mixing twenty-five pounds of oil of vitriol with ten pounds of water. A simple experiment, illustrative both of the evolution of heat by the combination of sulphuric acid with water, and of the power of the acid to absorb moisture from the air, consists in dipping the bulb of a thermometer in the concentrated acid, and then exposing it to the open air in a gentle draught: water is absorbed with sufficient rapidity to raise the mercury in the thermometer several degrees in the course of a few seconds.*

The existence of several definite combinations of sulphuric acid with water is now established beyond dispute:

1. The hydrate containing the smallest proportion

* The admixture of sulphuric acid with water in certain proportions has been suggested as a means of readily procuring any required temperature within a considerable range at a very short notice, but the rapidity with which the mixture afterwards cools is an inconvenience in this application of the acid. Several years ago Mr. Parkes constructed a small table to represent the degree of heat thus evolved; and though numerous similar experiments have been since executed, it is probable that his results have as much practical value as any others we possess, his experiments having been conducted on a very considerable scale. The acid employed was the common commercial oil of vitriol of specific gravity 1.844. The temperature of the acid was 56° Fahr., and that of the water and the atmosphere of the room in which the experiments

of water, is that in the Nordhausen acid, composed of two equivalents of anhydrous acid and one of water (see page 362). It may be regarded as a compound of the acid, containing one equivalent of water with the anhydrous acid.

2. The next is the common oil of vitriol, which is a compound of one equivalent of acid and one of water, when of the specific gravity 1.845 or thereabouts.

3. Acid of specific gravity 1.78 contains two equivalents of water to one of dry acid. When a more

were conducted was 50°. Fresh quantities of acid and water were employed for each experiment.

Heat produced by the admixture of sulphuric acid with water ; ten pounds of water being used in each experiment.

Sulphuric acid in pounds.	Temperature of the mixture in degrees of Fahrenheit.	Sulphuric acid in pounds.	Temperature of the mixture in degrees of Fahrenheit.
1	78°	13	229°
2	100	14	236
3	110	15	241
4	128	16	246
5	138	17	250
6	144	18	253
7	156	19	256
8	168	20	258
9	186	25	266
10	204	30	264
11	214	35	254
12	222	40	248

In making these experiments, observes Mr. Parkes, five minutes were required in the first two for the mixture to arrive at the maximum temperature ; afterwards it acquired the maximum in two minutes ; and when the weight of the sulphuric acid was more than half that of the water, the heat was evolved with still greater rapidity, until at last the change seemed to be instantaneous. In an experiment made upon ounces instead of pounds, the resulting temperature was considerably under that obtained on the larger scale : ten ounces of water at 50°, and thirty ounces of acid at 56°, gave on mixture in favourable circumstances a temperature of 246° instead of 264°.

dilute acid is concentrated by evaporation at a temperature not exceeding 400° Fahr., the water is reduced to the proportion in this hydrate; at a higher temperature the second equivalent of water is also expelled. When cooled to the freezing point of water, this hydrate forms large and regular crystals, and remains solid, according to Mr. Keir, till the temperature rises to 45° Fahr. (Phil. Trans. 1787.) During winter, accidents have sometimes occurred from the freezing of acid of this strength, the containing vessels being broken. If the acid contains the exact proportion of water, it freezes several degrees above the freezing point of water; but if the acid is of greater or smaller specific gravity than 1.78, so as to contain only 1 per cent. either more or less of real acid, it cannot be made to freeze above 32°.

4. The next hydrate is that which contains three equivalents of water to one of acid, and possesses the specific gravity 1.632. In whatever proportion concentrated sulphuric acid is mixed with water, a reduction of volume occurs, the bulk of the mixture being a trifle less than that of the acid and water separately. Now, the greatest condensation takes place when the acid and water are mixed in the proportion to form this hydrate; which is a sufficient proof of its being a definite chemical combination. It is also formed when a more dilute sulphuric acid is evaporated *in vacuo* at a temperature of 212°.

5. The existence of a hydrate containing six equivalents of water to one of dry acid, and of several definite hydrates containing a still larger proportion of water, is supported by recent thermometric researches.

It is often a matter of great importance to the manufacturer and the consumer of sulphuric acid to have a ready means of ascertaining the value and purity of a specimen of the acid, and also of preparing, at pleasure, an acid of particular strength. For all ordinary purposes the specific gravity is sufficiently indicative of the strength; and several valuable tables have been therefore constructed to exhibit at sight the quantity of real acid, or of concentrated acid (oil of vitriol), in dilute acid of different densities. Kirwan, Vauquelin, Dalton, Parkes, and Ure have each given a table for this purpose; the most reliance may be placed, I believe, on those by Mr. Parkes and Dr. Ure. The experiments of Mr. Parkes were performed on a large scale, and with extreme care to avoid all possible sources of fallacy. The temperature of the room in which they were performed was 60° Fahr., and the density of the oil of vitriol at that temperature 1.8494. Ten thousand grains of the acid were first well mixed with one hundred grains of water; the mixture was allowed to cool, and the specific gravity then observed. In the same manner the acid was diluted with other portions of water successively, the mixture being allowed to stand for some hours to cool before its density was ascertained. In those parts of the table to which an asterisk is attached, the results given are those of actual experiment, the others are deduced by calculation.

TABLE EXHIBITING THE QUANTITY OF REAL SULPHURIC ACID IN DILUTED ACID AT DIFFERENT DENSITIES. TEMP. 60° FAHR. BY MR. PARKES.

Parts of water mixed with 100 parts of sulphuric acid of 1·8494.	Specific gravity of the mixture.	Real acid per cent.	Parts of water mixed with 100 parts of sulphuric acid of 1·8494.	Specific gravity of the mixture.	Real acid per cent.
*1	1·8484	99·009	44	1·5937	69·444
*2	1·8465	98·039	*45	1·5879	68·965
*3	1·8445	97·087	46	1·5820	68·493
*4	1·8416	96·153	47	1·5761	68·027
*5	1·8387	95·238	48	1·5703	67·567
6	1·8358	94·339	49	1·5645	67·114
*7	1·8319	93·457	50	1·5585	66·666
8	1·8270	92·509	51	1·5526	66·225
9	1·8222	91·743	52	1·5478	65·789
*10	1·8163	90·909	53	1·5429	65·359
11	1·8104	90·090	*54	1·5390	64·935
12	1·8046	89·285	55	1·5351	64·516
13	1·7988	88·495	56	1·5312	64·102
14	1·7929	87·719	57	1·5273	63·694
*15	1·7880	86·956	58	1·5234	63·291
16	1·7821	86·206	59	1·5195	62·893
17	1·7744	85·470	60	1·5156	62·500
18	1·7666	84·745	61	1·5117	62·111
19	1·7588	84·033	*62	1·5078	61·728
20	1·7510	83·333	63	1·5039	61·349
*21	1·7431	82·644	64	1·5000	60·975
22	1·7353	81·967	65	1·4960	60·606
23	1·7275	81·300	66	1·4921	60·240
24	1·7207	80·645	67	1·4882	59·880
25	1·7138	80·000	68	1·4843	59·523
26	1·7070	79·365	69	1·4804	59·171
*27	1·7002	78·740	*70	1·4765	58·823
28	1·6933	78·125	71	1·4726	58·481
29	1·6865	77·519	72	1·4687	58·139
30	1·6796	76·923	73	1·4648	57·803
31	1·6728	76·335	74	1·4609	57·471
32	1·6660	75·757	75	1·4570	57·142
*33	1·6582	75·187	76	1·4531	56·818
34	1·6523	74·626	77	1·4502	56·497
35	1·6464	74·074	*78	1·4473	56·179
36	1·6406	73·529	79	1·4433	55·865
37	1·6348	72·992	80	1·4395	55·555
38	1·6289	72·463	81	1·4365	55·248
39	1·6230	71·942	82	1·4336	54·945
*40	1·6171	71·428	83	1·4306	54·644
41	1·6113	70·921	84	1·4276	54·347
42	1·6054	70·422	85	1·4257	54·054
43	1·5995	69·930	*86	1·4218	53·763

Specific gravity of acid at 15°C.	Parts of water mixed with 100 parts of sulphuric acid at 15°C.	Specific gravity of mixture	Real acid per cent.
1.1523	390	1.1523	21.739
1.1484	370	1.1484	21.276
1.1464	360	1.1464	20.833
1.1436	350	1.1436	20.406
1.1398	340	1.1398	20.000
1.1328	320	1.1328	19.230
1.1279	300	1.1279	18.518
1.1240	280	1.1240	17.857
1.1151	260	1.1151	17.241
1.1132	250	1.1132	16.666
1.1054	240	1.1054	15.284
1.0966	230	1.0966	14.285
1.0898	220	1.0898	13.333
1.0839	210	1.0839	12.500
1.0751	200	1.0751	11.764
1.0732	190	1.0732	11.111
1.0693	180	1.0693	10.526
1.0664	170	1.0664	10.000
1.0625	160	1.0625	9.523
1.0602	150	1.0602	9.090
1.0546	140	1.0546	8.333
1.0507	130	1.0507	7.692
1.0488	120	1.0488	7.142
1.0458	110	1.0458	6.666
1.0429	100	1.0429	6.250
1.0390	90	1.0390	5.882
1.0370	80	1.0370	5.555
1.0351	70	1.0351	5.263
1.0337	60	1.0337	5.000
1.0322	50	1.0322	4.761
1.0283	40	1.0283	4.255
1.0254	30	1.0254	3.846
1.0234	20	1.0234	3.508
1.0214	10	1.0214	3.225
1.0185	0	1.0185	2.777
1.0166		1.0166	2.439
1.0146		1.0146	2.173
1.0127		1.0127	1.960
1.0117		1.0117	1.785
1.0107		1.0107	1.639
1.0102		1.0102	1.515
1.0098		1.0098	1.408
1.0093		1.0093	1.315
1.0088		1.0088	1.234
1.0083		1.0083	1.162
1.0078		1.0078	1.098
1.0073		1.0073	1.041
1.0068		1.0068	0.990

TABLE OF THE QUANTITY OF OIL OF VITRIOL, OF SP. GR. 1·8485, AND OF REAL ACID, IN 100 PARTS OF DILUTE SULPHURIC AT DIFFERENT DENSITIES. BY DR. URE.

Oil of Vitriol.	Spec. Gr.	Dry Acid.	Oil of Vitriol.	Spec. Gr.	Dry Acid.	Oil of Vitriol.	Spec. Gr.	Dry Acid.
100	1·8485	81·54	66	1·5503	53·82	32	1·2334	26·09
99	1·8475	80·72	65	1·5390	53·00	31	1·2260	25·28
98	1·8460	79·90	64	1·5280	52·18	30	1·2184	24·45
97	1·8439	79·09	63	1·5170	51·37	29	1·2108	23·66
96	1·8410	78·28	62	1·5066	50·55	28	1·2032	22·83
95	1·8376	77·46	61	1·4960	49·74	27	1·1956	22·01
94	1·8336	76·65	60	1·4860	48·92	26	1·1876	21·20
93	1·8290	75·83	59	1·4760	48·11	25	1·1792	20·38
92	1·8233	75·02	58	1·4660	47·29	24	1·1706	19·57
91	1·8179	74·20	57	1·4560	46·48	23	1·1626	18·75
90	1·8115	73·39	56	1·4460	45·66	22	1·1549	17·94
89	1·8043	72·57	55	1·4360	44·85	21	1·1480	17·12
88	1·7962	71·75	54	1·4265	44·03	20	1·1410	16·31
87	1·7870	70·94	53	1·4170	43·22	19	1·1330	15·49
86	1·7774	70·12	52	1·4073	42·40	18	1·1246	14·68
85	1·7673	69·31	51	1·3977	41·58	17	1·1165	13·86
84	1·7570	68·49	50	1·3884	40·77	16	1·1090	13·05
83	1·7465	67·68	49	1·3788	39·95	15	1·1019	12·23
82	1·7360	66·86	48	1·3697	39·14	14	1·0953	11·41
81	1·7245	66·05	47	1·3612	38·32	13	1·0887	10·60
80	1·7120	65·23	46	1·3530	37·51	12	1·0809	9·78
79	1·6993	64·42	45	1·3440	36·69	11	1·0743	8·97
78	1·6870	63·60	44	1·3345	35·88	10	1·0682	8·15
77	1·6750	62·78	43	1·3255	35·06	9	1·0614	7·34
76	1·6630	61·97	42	1·3165	34·25	8	1·0544	6·52
75	1·6520	61·15	41	1·3080	33·43	7	1·0477	5·71
74	1·6415	60·34	40	1·2999	32·61	6	1·0405	4·89
73	1·6321	59·52	39	1·2913	31·80	5	1·0336	4·08
72	1·6204	58·71	38	1·2826	30·98	4	1·0268	3·26
71	1·6090	57·89	37	1·2740	30·17	3	1·0206	2·446
70	1·5975	57·08	36	1·2654	29·35	2	1·0140	1·63
69	1·5868	56·26	35	1·2572	28·54	1	1·0074	0·8154
68	1·5760	55·45	34	1·2490	27·72			
67	1·5648	54·63	33	1·2409	26·91			

The specific gravity of oil of vitriol, or acid of greatest concentration procured by evaporation, has

been differently estimated by different observers, which seems to proceed in some degree from the considerable change in bulk to which the concentrated acid is subject by an alteration in temperature. The following table contains a few of the experimental results obtained by Mr. Parkes in an investigation of this subject, an extension of which to temperatures above and below those selected may be found in his "Essay on Sulphuric Acid." During the experiments the barometer stood at 29·5 inches. No correction was made for the expansion and contraction of the glass vessel in which the acid was contained.

VARIATIONS IN DENSITY OF CONCENTRATED SULPHURIC ACID, THROUGH CHANGE OF TEMPERATURE.

Temperature, Fahrenheit.	Specific Gravity.	Temperature, Fahrenheit.	Specific Gravity.
30°	1·8593	56°	1·8500
32	1·8563	60	1·8468
36	1·8546	63	1·8449
38	1·8532	68	1·8435
40	1·8527	70	1·8430
42	1·8520	74	1·8413
44	1·8522	80	1·8381
46	1·8519	84	1·8343
48	1·8517		
52	1·8511		

Dr. Dalton observes, that "it is a mistaken notion, that the common sulphuric acid of commerce is of the maximum strength, though it is of the maximum density nearly. The fact is, acid nearly of the maximum strength varies very little in its specific gravity, by the addition or subtraction of a small quantity of water. The specific gravity ought not, therefore, to be the criterion of strength in acids above 70 per cent.; the temperature at which they boil is a much

better criterion, because it admits of a range of 12° or 15° for one per cent. of acid. Or the strength may be found by determining what quantity of water must be added to reduce the acid to some known strength, as that of the glacial acid of 1.78 specific gravity."

The following table, constructed by Dr. Dalton, exhibits the boiling points in degrees of Fahrenheit's scale of sulphuric acid of different strengths, from which the quantity of dry acid contained in a diluted acid may be estimated.

BOILING POINTS OF SULPHURIC ACID AT DIFFERENT STRENGTHS.

Specific Gravity.	Dry Acid per cent.	Boiling point.	Specific Gravity.	Dry Acid per cent.	Boiling point.
1.850	81	620°	1.769	67	422°
1.849	80	605	1.757	66	410
1.848	79	590	1.744	65	400
1.847	78	575	1.730	64	391
1.845	77	560	1.715	63	382
1.842	76	545	1.699	62	374
1.838	75	530	1.684	61	367
1.833	74	515	1.670	60	360
1.827	73	501	1.650	58.6	350
1.819	72	487	1.520	50	290
1.810	71	473	1.408	40	260
1.801	70	460	1.300	30	240
1.791	69	447	1.200	20	224
1.780	68	435	1.100	10	218

For manufacturing purposes it seldom happens that a more delicate test of the strength of sulphuric acid is required than that of its density or boiling point. The commercial acid, however, always contains small quantities of foreign matters, which may occasionally be present in sufficient proportion to increase its specific gravity, sufficiently to affect the hydrometer. Thus two and a half per cent. of sulphate of potash, a salt generally contained in small quantity in oil of

vitriol, increases the specific gravity 0.01. The presence of saline impurities of this kind may be detected by evaporating to dryness a given weight of the acid in a small platinum capsule, and weighing the fixed residue. The ordinary commercial acid generally leaves about one part of fixed matters for 250 parts of acid.

The most frequent impurities in the concentrated acid are sulphate of lead, arsenious acid, sulphate of tin, and nitric acid, nitric oxide or peroxide of nitrogen.

The sources of sulphate of lead are obviously the leaden chamber, and the leaden evaporating pans. The presence of this substance may be detected with facility by diluting the acid with several times its volume of water: if present, the acid then becomes turbid, sulphate of lead being insoluble in the diluted acid. By allowing the sulphate of lead to subside from the diluted acid, and decanting and evaporating the supernatant liquid, the acid may be obtained quite free from this impurity. This method of purification cannot be easily practised on the large scale, as it is necessary to effect the concentration entirely in vessels of glass or platinum. Sulphuretted hydrogen does not precipitate lead from the concentrated acid.

It rarely happens that sulphuric acid is met with in commerce quite free from a trace of arsenious acid. That deleterious substance is unfortunately present in considerable quantity in most specimens of the acid made from iron pyrites, which is the greatest objection to the use of that mineral as a source of sulphur. Arsenic is contained in a greater or smaller proportion in all varieties of pyrites, and becomes oxidized, by

the calcination, into arsenious acid, which, being volatile at a high temperature, is carried onwards with the sulphurous acid. Means are generally adopted, however, to condense the arsenious acid ere it reaches the chamber, by prolonging the pipe which leads from the sulphur burner into the chamber, so as to expose it to the cooling influence of the air. But a small portion still finds its way into the chamber to contaminate the acid. The acid manufactured from pure sulphur, however, also contains a trace of arsenic, though so minute as to require an exceedingly delicate test for its detection. Its source, in this case, is the metal of the chambers, and of the evaporating pans. The sheet-lead manufactured for sale in this country generally contains a small quantity of arsenic.

The best means of ascertaining the presence of arsenic in the acid is to evolve hydrogen gas from the diluted acid by means of a piece of pure zinc, or by electro-decomposition, and to observe whether a jet of the gas, when inflamed, affords a deposit of metallic arsenic on a cold substance, as a porcelain capsule, held *in* the flame. When zinc is used as the means of evolving hydrogen, it is essential to have the absence of arsenic in the metal previously demonstrated.*

Most specimens of oil of vitriol contain small traces of sulphate of tin, derived from the solder of the chambers, which is rapidly corroded by the acid. When the concentrated acid is diluted with from two to six times its weight of water, and treated with sulphuretted hydrogen, the tin falls as a brown sulphuret, mixed usually with the yellow sulphuret of arsenic.

* For a detailed account of the manner of conducting this operation, see Elements of Chemical Analysis, p. 116.

Besides the impurities already mentioned, concentrated sulphuric acid often contains a small quantity of one of the compounds of nitrogen and oxygen, probably peroxide of nitrogen in the form of the combination of that body with sulphurous acid, the presence of which is owing to the acid having been allowed to remain too long in the chamber. For some delicate chemical experiments, and for a few purposes in the arts, particularly the preparation of Saxon blue, commonly called sulphate of indigo, the acid must be carefully freed from this impurity. The best method of getting rid of the compound alluded to, is by diluting the concentrated acid with twice its bulk of water, and afterwards evaporating in the ordinary manner. The compound is then decomposed into nitric oxide which escapes as gas, and sulphuric acid. Mr. Blyth recommends that the sulphuric acid used for preparing sulphate of indigo should be withdrawn from the chamber for concentration at a spec. grav. not higher than 1.300 or 1.350.*

The most convenient method of freeing sulphuric acid, by one operation, from arsenious acid, sulphate of lead, and sulphate of tin, is by distillation. Many precautions are required in conducting this operation in a glass retort, from the violent jerks occasioned by the sudden production of vapour; but these may be prevented, to a great extent, by introducing into the retort some fragments of glass, or better, a few strips of platinum foil. By observing this precaution the production of vapour is greatly facilitated, and the acid boils quietly.

* Meeting of British Association, 1843. See a Report of Mr. Blyth's paper in the Athenæum.

The proper test for sulphuric acid, whether free or in combination with a base, is barytes. On adding a solution of any salt of that earth to a solution containing sulphuric acid or a sulphate, a white, heavy precipitate of sulphate of barytes is immediately produced, which may be distinguished from all other precipitates capable of being produced in a solution of barytes by its insolubility in nitric acid and muriatic acids.

The applications of sulphuric acid are so numerous and diversified as to render this article one of the most important of the objects of chemical manufacture. The production of many articles of considerable commercial importance is dependent to a greater or less extent on this acid, the cost of which exercises a great influence on the expense of carrying on some of the principal manufactures of this country. By far the most important application of sulphuric acid is the preparation of sulphate of soda from common salt, as the first part of the process for obtaining carbonate of soda from salt, which is fully described in the following article: the muriatic acid disengaged in this operation is usually collected and made available in the preparation of chloride of lime for the use of the cotton bleacher. The cost of sulphuric acid hence influences that of soda and all the articles in the manufacture of which that alkali is employed, such as soap, window-glass, and plate-glass: it also influences the cost of bleached and printed cottons, and all articles in the manufacture of which either muriatic acid or chlorine is employed. To a smaller extent sulphuric acid is used in dyeing and calico-

printing, hat-making, in refining silver, in tanning, in the manufacture of tin-plate, nitric and many other acids, blacking, stearine candles, alum, sulphate of ammonia, bichromate of potash, sulphate of copper or blue vitriol, various pigments, and a great number of other important articles of commerce. The quantity of oil of vitriol made annually in Great Britain is estimated at near sixty thousand tons.

THE SODA MANUFACTURE.

§ I. Sodium, Caustic Soda, and the Carbonates of Soda.—II. Barilla and Kelp.—III. Manufacture of Soda from Common Salt.—IV. Alkalimetry.

THE class of chemical bodies to which soda and potash belong is the alkalies, which are distinguished chiefly by their solubility in water, by their power of combining with acids and forming neutral saline compounds, and by their property of changing in a very remarkable manner the colours of certain vegetable matters. The word alkali is of Arabic origin, and is derived from *kali*, the name of a vegetable species from which soda was formerly extracted; the Arabic particle of perfection *al* having been prefixed to express the superiority of the alkali over the plant which afforded it. Excepting the vegetable alkalies or alkaloids, such as morphine and quinine, which are met with only in vegetables, and are peculiar to certain genera, only four proper alkalies are known at present, namely, ammonia, potash, soda, and lithia. The first of these, being, in its pure state, a gas at all common temperatures and pressures, is designated the *volatile* alkali, in contradistinction to the remaining three, which are the *fixed* alkalies, they not being at all volatile at a red heat. Lithia has hitherto been found only in a few scarce minerals, and it has received no application in the arts.

When an infusion of litmus, which has been reddened by a few drops of an acid solution, is mixed with a slight excess of an alkali, the colour of the infusion changes to purple or blue; by applying an excess of acid to the same infusion, the original red colour is restored. In like manner the purple infusion obtained by macerating red cabbage in hot water, and also the infusion of the petals of the red rose, become green by the addition of an alkali, and crimson by that of an acid. Turmeric and many other yellow dyes are rendered brown by an alkali, but the original yellow is restored on applying an acid. Alkaline carbonates produce the same effects on vegetable colouring matters as the caustic or pure alkalies.

A class of bodies distinguished as *alkaline earths*, to which belong lime and barytes, act on such colouring matters in precisely the same manner as alkalies, which they also resemble in some other respects. The distinction between an alkali and an alkaline earth is founded merely on the solubility or insolubility of the carbonate of the base in water; the carbonate of an alkali proper being soluble, and that of an alkaline earth insoluble.*

§ 1. SODIUM, CAUSTIC SODA, AND THE CARBONATES OF SODA.

Sodium, the metallic basis of soda, was first obtained by Sir H. Davy, in 1807, by subjecting moist-

* In like manner, the distinction between an alkaline earth and an earth proper, as alumina, is founded on the solubility or insolubility of

ened hydrate of soda to voltaic decomposition, when the oxygen both of the water and the soda were liberated at the positive pole, and the sodium of the latter at the negative pole. A more advantageous method of procuring this metal has since been devised, which consists in strongly heating in an iron distillatory apparatus an intimate mixture of carbonate of soda and charcoal. The oxygen of the soda unites with the charcoal; while the liberated sodium, being volatile at a red heat, rises in vapour and is condensed in the receiver, which should contain rectified naphtha or petroleum to preserve the sodium from oxidation by the air.*

Sodium has considerable lustre, and in colour is very similar to silver. Its specific gravity, according to Gay-Lussac and Thénard, is 0.972 at 59°. At common temperatures, it is sufficiently soft to be reduced to thin leaves by the pressure of the fingers. It is liquid at 200°, but does not rise freely in vapour under a bright red heat. It presently becomes tarnished on exposure to the air, owing to the formation of a crust of soda; and takes fire and emits

the base itself; alkaline earths are more or less soluble, but earths proper are quite insoluble.

* For a description of the proper apparatus for preparing the metallic bases of the fixed alkalies, see Graham's "Elements of Chemistry," p. 440.

The following mode of obtaining sodium is recommended by M. Schœdler. Three pounds of commercial acetate of soda are ignited, the free access of air being avoided; and the residue of carbonate of soda and charcoal, which weighs about one pound, is mixed with a quarter of a pound of finely powdered charcoal and half a pound of charcoal in a coarser state, to prevent fusion of the mass. The mixture, when heated in the usual manner in one of the iron bottles in which mercury is imported, should yield between four and five ounces of pure sodium.

brilliant scintillations when heated nearly to redness. When thrown on water, it oxidates with great vivacity; hydrogen gas is disengaged, and an alkaline solution of soda formed: on cold water it does not inflame as potassium does, but on hot water it scintillates and sometimes takes fire. If moistened with only a few drops of cold water, it becomes sufficiently hot to inflame.

The commonly received equivalent of sodium is 23.3. Its symbol is Na (from *natrium*). Sodium forms at least two compounds with oxygen; one of which, the basis of common soda, contains one equivalent of metal to one of oxygen; the other oxide is a peroxide, possessing neither acid nor alkaline properties, composed of two equivalents of sodium to three equivalents of oxygen. The peroxide is decomposed by contact with water into soda and oxygen gas.

Soda.—Pure soda, free from water, can only be obtained by the combustion of pure sodium in dry air or oxygen gas. The solid residue of the evaporation of a solution of caustic soda (soda ley), retains one equivalent of water to one equivalent of soda, even when heated to redness.

Anhydrous soda is a grey solid, of difficult fusibility, having a very powerful affinity for water. The hydrate is white and brittle, very caustic, possessed of powerful alkaline properties, easily fused by heat, and readily dissolved by water and alcohol. Its specific gravity is 1.536. At a very elevated temperature it is dissipated as a vapour. A solution of caustic soda dissolves wool, hair, the skin, and most

animal matters; tallow and other unctuous matters, with the formation of soaps; sulphur and some metallic sulphurets; silica, alumina, and several metallic oxides quite insoluble in water.

Solution of caustic soda is always prepared by decomposing carbonate of soda by means of caustic lime in the presence of water. The lime then unites with the carbonic acid of the alkaline carbonate to form carbonate of lime, and alkali is left in a state of causticity.*

In preparing soda leys on an extensive scale, where absolute purity is not essential, as in the soap manufacture, the mixture of lime and carbonate of soda or soda-ash is placed in large cast-iron vats and covered with water, and after some hours, the ley is withdrawn through a plug at the bottom of the vat, and either fresh water or a weak ley introduced at top. (See the description of the mode of preparing soda leys for the soap manufacture in the article on Soap, p. 300.)

A much purer ley may be prepared by boiling in a clean iron pot a solution of two parts of crystallized carbonate of soda in eight or ten parts of water, with about one part of hydrate of lime, until a little of the liquid from which the insoluble carbonate of lime has been separated by subsidence and decantation ceases to effervesce when saturated by an acid. The pot may then be removed from the fire, carefully covered to prevent the ley from absorbing carbonic acid from the air; and when the insoluble carbonate of lime and

* The power of lime to decompose alkaline carbonates is perceived on mixing clear lime-water with a clear solution of carbonate of soda or potash, when an immediate precipitation of carbonate of lime appears.

the excess of hydrate of lime have subsided, the clear ley may be decanted into stoppered vessels for use, or be evaporated in an iron or silver vessel until it assumes an oily appearance, and then be poured upon an iron or stone slab or into iron moulds to solidify. The access of air should be avoided as much as possible during the concentration of the ley.

The solution of soda made as above from soda-ash is contaminated with common salt and sulphate of soda, both of which may be separated by concentrating the solution considerably, these salts being insoluble in a strong solution of soda.

The following table, founded on the experiments of Richter, exhibits the proportion of *hydrate of soda* and of *dry caustic soda* contained in leys at different densities :

SOLUTION OF CAUSTIC SODA.

Density of the solution.	Dry soda per cent.	Hydrate of soda per cent.	Density of the solution.	Dry soda per cent.	Hydrate of soda per cent.
1.00	0.00	0.00	1.22	16.05	20.66
1.02	1.61	2.07	1.24	17.44	22.58
1.04	3.12	4.02	1.26	19.00	24.47
1.06	4.80	5.89	1.28	20.45	26.33
1.08	5.87	7.69	1.30	21.87	28.16
1.10	7.32	9.43	1.32	23.27	29.96
1.12	8.62	11.10	1.34	24.60	31.67
1.14	9.95	12.81	1.35	25.16	32.40
1.16	11.44	14.73	1.36	25.69	33.08
1.18	12.99	16.73	1.38	26.73	34.41
1.20	14.44	18.71			

Carbonate of soda.—The common mode of manufacturing this useful salt for commercial purposes forms the subject of another section of the present article. Its chemical history may be conveniently considered here.

The soda crystals (common soda) of commerce are crystallized carbonate of soda nearly pure, the only foreign matters being about one half per cent. of sulphate of soda (Dr. Thomson), and an almost inappreciable trace of iron. The crystals, when formed near the common temperature, are composed of one equivalent of the dry carbonate and ten equivalents of water, or, in 100 parts, of 21.81 soda, 15.43 carbonic acid, and 62.76 water. When exposed to the air, they fall to powder, and at the same time lose a portion of their water of crystallization. According to Dr. Thomson, 100 parts of water dissolve 20.64 parts of the crystals at 58°.25, and more than an equal weight at the boiling temperature: the solution has a strong alkaline taste and reaction. When moderately heated, the crystallized carbonate undergoes the *watery fusion*; the whole of its water is soon expelled, and the anhydrous carbonate remains as a white pulverulent mass, which again becomes liquid as the heat is increased to redness (then undergoing the *igneous fusion*), without parting with any portion of its carbonic acid.

The crystals of carbonate of soda formed at a temperature about 80° contain seven equivalents of water instead of ten, and are not efflorescent. The crystals deposited on the cooling of a solution saturated between 68° and 86° have been found to contain 17.74 per cent. of water, which nearly corresponds to one equivalent and a quarter. The pulverulent salt precipitated on evaporating a solution of carbonate of soda at the boiling point contains about the same proportion of water.

The soda-ash of commerce is dry carbonate of soda,

contaminated with variable quantities of common salt and sulphate of soda, and sometimes with sulphuret of sodium, carbonate of lime, and iron in a soluble state, probably as sulphuret in combination with sulphuret of sodium. A process for determining the proportion of real alkali will be afterwards described.

A ready means of detecting the presence of caustic soda in the soda-ash of commerce is occasionally of some importance in the chemical arts. A convenient test for this purpose is a solution of nitrate of silver, which gives a *white* precipitate with a solution of an alkaline carbonate containing no caustic alkali, but a *brown* precipitate with a caustic alkali, or a mixture of a caustic and carbonated alkali.

Carbonate of soda is frequently found as an efflorescence in delicate needles upon damp walls, being probably produced by the action of the lime in the mortar on common salt. An intimate mixture of caustic lime and common salt, kept in a moist state and exposed to the air, also yields, after a long time, a slight efflorescence of carbonate of soda, but the action is too slow to allow of such a process being made available in the manufacture of the carbonate.

Sesquicarbonate of soda.—This salt, which is a natural product, and hence sometimes called *mineral soda*, is intermediate in composition between the carbonate and bicarbonate of soda, being composed of two equivalents of soda and three of carbonic acid, with three equivalents of water (M. Hermann). It is less soluble in water than the carbonate, and more soluble than the bicarbonate, and does not effloresce on exposure to the air. At the soda lakes in the

province of Sukena in Africa, this salt forms a striated crystalline stratum, just below the surface. From these lakes several hundred tons are collected annually in the dry season, chiefly for consumption in Africa; but some is exported to Europe, and sold under the name of *trona*. Hungary, Mexico, and Columbia also possess productive soda lakes.*

Bicarbonate of soda.—This salt is prepared, on the large scale, by exposing pounded soda crystals, or else an intimate mixture of four parts of effloresced carbonate and one part of crystallized carbonate, to an atmosphere of carbonic acid gas; and not, as commonly stated, by transmitting a stream of carbonic acid gas through a saturated solution of the neutral carbonate. The carbonic acid may be derived by the decomposition of chalk by sulphuric or muriatic acid, or from a liquor undergoing the vinous fermentation. The latter method may be advantageously practised in distilleries, where a great quantity of liquor is kept in a fermenting state for a considerable time. With proper precautions a charcoal fire might be

* According to M. Hermann, the sesquicarbonate of soda cannot be prepared pure by crystallization from an aqueous solution; as it decomposes when in solution into the bicarbonate and carbonate of soda, which crystallize apart. When a concentrated solution of bicarbonate of soda is evaporated quickly, so as to avoid the dissipation of the whole of the second equivalent of carbonic acid; when the bicarbonate and crystallized carbonate are mixed in single equivalent proportions, and the mixture is made to undergo the watery fusion; and lastly, when the bicarbonate of soda is exposed to heat, the temperature not being allowed to exceed 482° Fahr., products are obtained which consist, for the most part, of the sesquicarbonate. If these masses are exposed for a few weeks to a humid atmosphere, they assume a perfectly crystallized structure, and their cavities and fissures become lined with groups of crystals, which are pure crystallized sesquicarbonate of soda. (Chemical Gazette, No. VI.)

made available as the source of carbonic acid. The soda which remains in the state of neutral carbonate may be removed by washing the mixture with cold water.*

Bicarbonate of soda has an alkaline reaction, although it contains two proportions of carbonic acid to one of soda. Its taste is much milder, however, than that of the neutral carbonate, being scarcely perceptible when mixed with a little common salt. It dissolves in about ten times its weight of water at 60°. At the boiling temperature, it slowly disengages carbonic acid gas, becoming at length reduced, according to Rose, to the neutral carbonate. When pure, it contains in 100 parts, 37 (1 eq.) soda, 52·3 (2 eqs.) carbonic acid, and 10·7 (1 eq.) water. As met with in commerce, it generally contains more than 40 per cent. of soda, owing to the presence of neutral carbonate of soda with 1 eq. or $1\frac{1}{4}$ eq. of water of crystallization. The presence of the neutral carbonate may be detected by the formation of a precipitate, when the solution of the suspected bicarbonate is mixed with a solution of sulphate of magnesia: pure bicarbonates of the alkalies produce no precipitate, in the cold, with solutions of salts of

* The rapidity with which effloresced carbonate of soda absorbs carbonic acid gas is said to be considerably increased by mixing with the carbonate, recently calcined and powdered, charcoal made from soft wood, which possesses the power of condensing gases within its pores to an extraordinary extent. The mixture, which may be made in the proportion of two parts of effloresced carbonate and one part of charcoal, is moistened, exposed to the gas for twenty-four hours, then taken out, powdered and moistened, and again exposed to the gas. These operations having been twice repeated, the mass is mixed with eight parts of hot water, the solution is filtered while hot, and left for the bicarbonate to crystallize (M. Artus, Chemical Gazette, No. XIV).

magnesia; but if heat is applied, carbonate of magnesia is precipitated. The alkaline carbonate contained in mineral waters, such as those of Seltzer, Carlsbad, and the Azores, is chiefly bicarbonate of soda.

§ II. BARILLA AND KELP.

Until within the last twenty years nearly all the soda required for purposes of commerce was obtained by incinerating marine plants. The residuary ash prepared on the Mediterranean shores and other warm climates, where the plants chiefly operated on are the *salsola soda* and the *salicornia herbacea*, is barilla; that prepared on the coasts of Ireland and the western coasts and islands of Scotland from the *fucus vesiculosus* and other species of fuci, is kelp, which is considerably inferior to barilla in value.

Barilla, of good quality, contains about one-fifth of its weight of soda, in the state of carbonate; the remainder being sulphate of soda, chloride of sodium, earthy and carbonaceous matters, and a little sulphuret of sodium and sulphite of soda. The best barilla is that brought from Alicant, in the neighbourhood of which place it was formerly prepared in great quantities from the *salsola soda*, which is cultivated for this purpose on the eastern shores of Spain. The plants are raised from seed (the exportation of which is said to be punishable with death) sown at the close of the year, and are in a fit state to be gathered in the month of September following. After having been dried in heaps, their seeds are rubbed out, and the rest of the plants is burned in

furnaces, at a temperature sufficient to bring the ash into a state of semi-fusion. When cold, the ash forms a hard, dry, spongy mass of a blueish-grey colour.

The quantity of barilla retained for home consumption in the United Kingdom, on the average of the five years ending with 1834, amounted to 12,600 tons; at present, however, the importation of barilla into this country is almost discontinued, in consequence of the extensive scale on which the manufacture of soda from common salt is now carried on. The duty on barilla was reduced in 1822 from 11*s.* 4*d.* to 8*s.* 6*d.* per cwt., in 1831 to 2*s.* per cwt., and in 1842 to 3*d.* per cwt.

The manufacture of kelp has long been carried on on the north and west coasts of Ireland, from whence it was introduced, about the middle of last century, to the western shores and islands of Scotland. During the imposition of the high duties on barilla and common salt, to meet the exigencies of the late war, the kelp manufacture afforded very considerable revenues to the proprietors of the Scottish shores; the annual rental of the kelp-shores of the island of North Uist alone amounted to 7000*l.*, and at one period the entire quantity of kelp produced in Scotland and its adjacent islands was estimated at more than twenty-five thousand tons annually. The price of the kelp was sometimes so high as twenty pounds per ton, but the average price during twenty-two years ending with 1822, was ten guineas. The repeal of the duty on salt, which has allowed the manufacture of soda from that source, has put an almost entire stop to the kelp manufacture; and hence shores that formerly afforded their proprietors an annual rental

of four or five hundred pounds are now all but valueless.

The composition of kelp is very variable, not only as regards the proportion of carbonate of soda, but of the other constituents; hence the uncertainty which attended its employment in some of the chemical arts, particularly in the manufacture of crown-glass. The proportion of pure carbonate of soda varies from two to seven per cent.; the other constituents soluble in water are common salt, chloride of potassium, sulphate of soda, sulphuret of sodium, and traces of iodide of sodium. The insoluble matters, which usually form about one-half the weight of the kelp, consist chiefly of carbonate of lime, alumina, silica, and sulphate of lime. The proportion of alkaline carbonate may be increased to some extent by conducting the incineration at a higher temperature than usual; but kelp is now valued more for its chloride of potassium and traces of iodine than for its alkaline carbonate, and a high temperature is attended with the loss of the iodide of sodium, in consequence of its volatility.*

* To separate the iodine and chloride of potassium, the broken kelp is lixiviated with water, and the solution is evaporated in an open pan. When the solution is concentrated to a certain point, it begins to deposit, while boiling, its common salt, carbonate of soda, and sulphate of soda, which are removed on a perforated shovel, and the liquid is run into a shallow pan to cool, where it deposits crystals of chloride of potassium. The mother-liquor is subjected to a repetition of these operations to obtain more crystals; and the last mother-liquor, which is a dense dark-coloured liquid, containing nearly the whole of the iodide of sodium, is alone employed in the preparation of iodine. For this purpose, it is merely heated in a peculiar distillatory apparatus with sulphuric acid and black oxide of manganese, or else with sulphuric acid only. A detailed account of this process is contained in Professor Graham's "Elements of Chemistry," p. 384.

§ III. MANUFACTURE OF SODA FROM COMMON SALT.

The common process for obtaining soda by the decomposition of sea-salt, which is scarcely second in importance to any manufacturing process at present practised, was invented by M. Leblanc, a French chemist, towards the close of last century. The supply of Spanish barilla being cut off from France during the cessation of the commercial intercourse between France and Spain at the time of the French Revolution, the National Convention made an appeal to the chemists of France to devise a process in which common salt might be made available as a source of soda. Of all the processes communicated to the committee entrusted with the examination of the various proposals, the only one deemed likely to be advantageous was that of Leblanc, which was precisely the same in principle as the soda process now practised on a prodigious scale, both in this country and in France. The first establishment for prosecuting this manufacture was erected in 1804 at Saint-Denis, by Leblanc, with funds afforded him by the *Société d'Encouragement*. The British Government gave Leblanc a handsome reward for his invention; but he was neglected by the Government of his own country, and after having expended his whole property in bringing his process to perfection, at last died in a hospital* (M. Girardin).

The enormous duty on salt, to the amount of fifteen shillings per bushel, or about thirty times the

* It is said that statues of M. Leblanc have been erected at Greece and Rome.

cost of the salt, with which this country was taxed from 1805 until 1823, effectually prevented the general introduction, during that period, of the soda process of Leblanc. But since the entire repeal of the salt duty, or rather within the last fourteen or sixteen years, the soda manufacture has experienced a wonderful developement in this country: the kelp of Scotland is now valueless as a source of soda; barilla is an article almost unknown in our markets; and the united quantity of soda-ash and soda crystals annually manufactured from salt probably exceeds seven times the greatest importation of barilla ever made in one year.

The materials used in the soda manufacture are common salt, sulphuric acid, small coal or slack, chalk or broken limestone, and charcoal.

Common or *sea salt*, sometimes improperly designated muriate of soda, is a combination of two elementary substances, chlorine and sodium, in the proportion of 1 eq. (35 parts by weight) of the former, and 1 eq. (23 parts) of the latter. Its proper designation is therefore chloride of sodium. It contains no water of crystallization, and may be obtained in its ordinary state by exposing sodium to chlorine gas, when the metal takes fire spontaneously. Chloride of sodium is also formed in a state of purity when hydrochloric or muriatic acid is neutralized with soda or its carbonate; in which case the hydrogen of the hydrochloric acid unites with the oxygen of the soda, and the chlorine of the acid with the sodium.*

* The most important characters and properties of common salt are the following. It crystallizes from its solution in water in cubes, and

The great sources of common salt are two, either of which is inexhaustible: the sea, and the beds of rock-salt or sal-gem. Sea-water contains nearly 3 per cent. of common salt, which is by far the most considerable of its saline constituents. Salt is obtained from this source, in warm climates, by spontaneous evaporation; the water being contained in shallow basins, called brine-pits, excavated along the sea-shore: but in cooler climates the evaporation is assisted by heat artificially applied. The uncrystallizable mother-liquor, or *bittern*, obtained in this process is valued just as highly as the salt, on account of its containing a considerable quantity of chloride of magnesium, which is made available in the preparation of Epsom salts and carbonate of magnesia. The most advantageous sources of salt

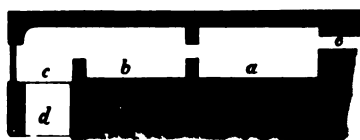
from urine and liquids containing phosphates in regular octohedra. When its solution is evaporated rapidly, it crystallizes in hollow four-sided pyramids on the surface of the saline solution; the apex, which is a single cubical crystal, being downwards. The sides of the pyramid consist of lines of small cubes deposited successively on the upper edges of the floating crystal. When a saturated solution is cooled down to a temperature between 14° and 5° Fahr., the salt crystallizes in hexagonal tables, containing, according to Fuchs, six equivalents of water. When these crystals are allowed to rise in temperature above 14° , they undergo decomposition, part with water, and become converted into a congeries of minute cubes. When heated, crystals of common salt decrepitate, from the expansion of water confined between their plates; at a bright red heat they enter into a state of fusion, and at a higher temperature rise in vapour. Some kinds of rock salt do not decrepitate. It is remarkable that pure common salt has exactly the same degree of solubility in hot and cold water; according to Fuchs, 100 parts of water dissolve 37 parts of pure salt at all temperatures; but salt contaminated with chloride of magnesium is more soluble. It is nearly insoluble in absolute alcohol, but dissolves easily in rectified spirits. It deliquesces slightly in a damp atmosphere, but not when the air contains no more than its ordinary proportion of aqueous vapour.

in this country are the beds of rock-salt and the salt-springs in Cheshire, Worcestershire, and Staffordshire. Rock-salt is sometimes met with perfectly colourless and transparent, and sufficiently pure for all the ordinary uses of salt; but it usually has a reddish-brown colour, due to the presence of clay, from which it may be freed by solution in water, subsidence, and decantation (or filtration), and evaporation of the clear solution. Instead of mining the salt in the usual manner, water is frequently admitted to the bed of salt through a bore from the surface; and the brine thus formed is drawn off by means of a pump and a copper pipe of a few inches in diameter, suspended in the bore. The earthy impurities are separated from the brine by subsidence and decantation, or by filtration, and the clear solution is evaporated to obtain crystals. The salt prepared from either of these sources is never perfectly pure; but the impurities, which are chiefly sulphate of lime, chloride of magnesium, and sulphate of magnesia, seldom amount to as much as two per cent. The quantity of common salt at present consumed in the alkali works of this country is estimated to fall little short of seventy thousand tons per annum.

The first branch of the soda manufacture consists in the conversion of common salt into sulphate of soda by the application of sulphuric acid. This is effected in a reverberatory furnace, technically called the "decomposing furnace." Some furnaces of this kind have two compartments, in one of which is conducted the evaporation of the liquid, and in the other, the calcination of the residuary sulphate; but in many "de-

composing furnaces," the evaporation and calcination

Fig. 43.



are effected in the same division. Fig. 43 represents a perpendicular section of a furnace of the first kind; *a* is called the "decompos-

ing bed," and *b* the "roasting bed:" in *a* the salt and sulphuric acid are mixed, and the solution evaporated, until the residuary sulphate has a pasty consistence; in *b* the desiccation of the sulphate is completed: *c* is the fire-place, *d* the ash-pit, and *e* the flue, which communicates with a tall draught chimney. In some alkali works a rectangular leaden pan, of from five to eight inches in depth, is placed upon the decomposing bed *a*, to receive the salt and sulphuric acid; the part of the side of the pan opposed to the small opening for withdrawing the pasty sulphate is sloped outwards a little, to form a kind of spout, and the aperture is closed, during the operation, by bricks, luted with clay. In general, however, the salt and sulphuric acid are laid directly upon the decomposing bed, which is made water-tight with cement.

A fire having been kindled in *c*, and the proper quantity of salt introduced (which may vary from two or three hundred-weight to half a ton, according to the size of the furnace), an equal weight of sulphuric acid of sp. gr. 120° Twaddell (1.600) is poured upon the salt through an aperture in the roof of the furnace, closed at other times with a leaden plug; or the acid may be conveniently introduced through fixed siphon funnels made of lead. When the acid and

salt are mixed in the above proportion, which is I believe the most common, the salt is in considerable excess, as six parts of pure salt require for complete decomposition exactly seven parts, by weight, of sulphuric acid of 120° Tw. Some soda manufacturers employ a stronger, and others a weaker acid than the above; the proportion of acid being varied accordingly, so as to have a constant proportion of real acid: the extremes should not exceed 140° Tw. (1.700) on the one side, and 110° Tw. (1.550) on the other. The acid should be poured in upon the salt slowly, and the mixture be equalized, by stirring with an iron rake coated with sheet-lead.

As soon as the acid and salt are placed in contact, abundant fumes of muriatic or hydrochloric acid are disengaged from the mixture, and conveyed through the flue either directly up the chimney, and suffered to go to waste, or else through a condenser containing water, for the purpose of procuring the acid in the form of liquid muriatic acid, or the spirits of salt of commerce, which is a concentrated aqueous solution of the acid. The evolution of muriatic acid continues until the sulphate is perfectly dry.

The reaction which takes place between sulphuric acid and common salt may be easily understood with the assistance of the annexed diagram: for simplicity, the acid is supposed to be strong oil of vitriol, that is, sulphuric acid, containing only one equivalent of water.

REACTION OF OIL OF VITRIOL ON COMMON SALT
(CHLORIDE OF SODIUM).

Before decomposition.		After decomposition.	
58.3 chloride of sodium	{ 35 chlorine 23.3 sodium	36 hydrochloric acid.	71.3 sulphate of soda.
49 oil of vitriol	{ 1 hydrogen 8 oxygen 40 sulphuric acid		

From which it appears, that 58.3 parts of common salt should afford, when sufficient sulphuric acid is employed, 71.3 parts of dry sulphate of soda. But so large a quantity of the sulphate is rarely, if ever, obtained on the large scale; because the acid is not applied in sufficient quantity to decompose the whole of the salt. An excess of salt, however, is a much smaller inconvenience than an excess of sulphuric acid.

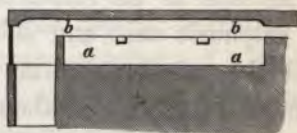
To effect the condensation of the muriatic acid gas evolved from the mixture of salt and sulphuric acid, the current of gaseous acid and smoke is brought into contact with a gentle stream of water flowing in the opposite direction, over an extensive surface. For this purpose, the chimney into which the flue *e* leads may be filled with rounded flints, kept constantly wet by a small stream of water from the top; a pipe being placed at the bottom of the chimney to conduct the liquid into a subterranean reservoir. The condensation of the acid may be more conveniently effected by conducting the fumes into a condenser, consisting of a series of upright channels, or flues, in which the fumes alternately ascend and descend. Water is allowed to fall into these channels from above, and be

distributed over boards placed obliquely, or any other convenient surface; or the water may be admitted at bottom, in the form of a fountain, supplied from a reservoir on the top of the condenser. If the pipes for conveying the water from the reservoir to the bottom of the condenser are placed within the condenser, they should be made of glazed earthenware. A condenser of this kind was made the subject of a patent by Mr. Lawrence Rowe, in 1839.

As the transmission of the current of acid fumes and smoke through a condenser materially interferes with the draught, an arrangement is adopted at some alkali works for conveying the acid fumes into a condenser apart from the smoke. With this view the sulphuric acid and salt are sometimes mixed in a shallow iron basin, supported over a fire-place, and surmounted by a dome of brick-work, from the top of which proceeds a pipe to conduct the muriatic acid to a condenser. At the bottom of the brick dome is an opening through which the materials are introduced, and at the bottom of the iron basin is another opening for the extraction of the residuary sulphate of soda. Fig. 44 represents the perpendicular

section of a single-bedded decomposing furnace, so constructed as to prevent the inter-

Fig. 44.



mixture of the muriatic acid with the smoke: *a a* is the decomposing bed; the salt and sulphuric acid are introduced through a door at one side, and the muriatic acid is led into a condenser by a pipe proceeding from the other side: the smoke passes

into a chimney through the arched flue *b b*, the bottom of which is as wide as the decomposing bed. The flue is separated from the decomposing bed by cast-iron plates and slate stones supported by iron bearers.

As the consumption of muriatic acid bears a small proportion to that of soda, many alkali manufacturers consider it to be to their advantage to allow the acid vapours to escape entirely, the inconveniences which attend the condensation of the acid being of greater consequence than the value of the liquid acid. Some means of condensation, however, should always be applied where the works are situated in or near a cultivated district; as the acid vapours, if allowed to escape into the air, never fail to sterilize the surrounding vegetation. In many places, the vapours might easily be conveyed to a vault through which a current of water might be conducted to a neighbouring river. To carry off the smoke and uncondensed gases, and to maintain a proper draught in the furnaces, a chimney might be erected over the farther end of the vault, provided no ingress is allowed for air except through the furnaces.

As soon as the fumes disengaged from the mixture of sulphuric acid and salt cease to be very copious, and the mixture attains a pasty consistence, which generally happens in about two hours from the time of charging, the mass is pushed out of the decomposing bed, through the opening at the back of the furnace, into a place supplied with a dome or chimney for the purpose of carrying off the acid vapours, which would suffocate the workmen if diffused into the air. The fire in the furnace having been checked a

little, another charge is introduced into the decomposing bed in the same manner as before; after which the product of the first charge, by this time somewhat cooled, is shovelled into the "roasting bed," *b*, fig. 43. There the sulphate is exposed to a much higher degree of heat, which serves, in an hour or so, to dissipate all traces of muriatic acid. When it has ceased to emit acid fumes, and has changed from a yellowish colour to white, it may be raked out of the furnace to make room for another charge. The dry sulphate is technically known by the name of "salt cake."

Several other methods of procuring sulphate of soda for the alkali manufacture have been proposed, but neither of them has yet come into successful competition with the above. Sulphate of iron (copperas), which may be obtained at a very moderate expense by the oxidation of iron pyrites, may be made available in the conversion of common salt into sulphate of soda, in two ways:

1°. By calcining at a red heat an intimate mixture of the two salts (in the proportion of single equivalents) in a reverberatory furnace, when the volatile perchloride of iron is disengaged, and a mixture of sulphate of soda and peroxide of iron left as a residue, from which the sulphate may be separated by water. This mode of procuring sulphate of soda has long been proposed, but a few years since it was made one of the subjects of a patent for this country.

2°. By dissolving copperas and salt together in water, when a double decomposition takes place, with formation of sulphate of soda and chloride of iron. The former may be obtained in hydrated crystals by exposing the solution to a low temperature; or in the

anhydrous state, as an opaque precipitate, by concentrating the solution at the boiling point.* In either case the chloride of iron remains in the mother-liquor.

Common salt has also been converted into sulphate of soda by the agency of sulphate of magnesia. When these two salts are mixed in solution, a double decomposition takes place, and sulphate of soda may be separated from the liquor, either by exposure to cold, or by concentration at the boiling point. Chloride of magnesium remains in the mother-liquor.

Another method is by the calcination of a mixture of common salt and finely-powdered pyrites. One hundred parts of pyrites are mixed with forty parts of common salt, and roasted in a proper furnace for sixty hours; the brownish-red mass which results is lixiviated in water, and the solution evaporated to afford crystals. The product consists of about forty-five parts of crystallized sulphate, which correspond to about twenty parts of dry sulphate. The addition of carbonaceous matter is said to accelerate the process, and increase the product. (Brande's *Manual*.)

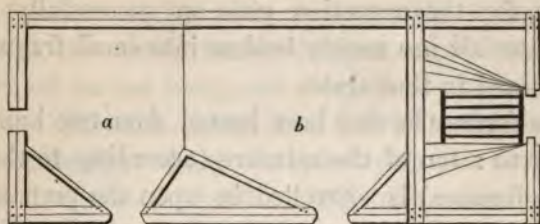
The sulphate of soda being obtained, the next step in the process consists in calcining it with chalk or broken limestone, and small coal.

The furnace in which this operation is conducted is called the "fluxing" or "black ash furnace." It is quite similar to a common reverberatory; but its

* Sulphate of soda is considerably less soluble in water at the boiling point than at some degrees below: at the temperature 91° Fahr., 100 parts of water dissolve 50·65 parts of the anhydrous sulphate, but at the boiling temperature only 42·65 parts.

floor is divided into two parts, one of which, the farthest from the fire, is four or five inches higher than the other. The annexed figure is a horizontal

Fig. 45.



section, or ground-plan, of a furnace of this kind: *a* is called the “preparatory bed,” because the cold materials are first placed there, and thoroughly heated, to avoid cooling the furnace, when the mass is afterwards placed on *b*, which is called the “fluxing bed.” The preparatory bed and fluxing bed have each a door-way in the side of the furnace, and a small peep-hole through the door to view the progress of the operation. The usual length of black-ash furnaces is from eighteen to twenty feet, and the breadth from eight to ten feet. The “fluxing bed” sinks towards the centre to the depth of one inch and a half.

The proportions in which the mixture of sulphate of soda, limestone or chalk, and coal is made, are varied at different works; but the success of the operation is influenced to a considerable extent by the exactness observed in the ratio. In an extensive alkali work at St. Helen’s in Lancashire, the proportions taken are thirteen parts of salt cake, nine and a half parts of coal, and fourteen parts of limestone. Dr. Ure recommends ten parts of the sulphate, from eleven to twelve parts of chalk or limestone, according

to its purity, and five parts of coal. In some alkali works the materials are ground and sifted separately, and then carefully mixed; but the trouble of grinding and sifting may be avoided without much inconvenience, for the operation goes on successfully when the materials are merely broken into small fragments, and mixed in that state.

The furnace having been heated, from two hundred-weight to a ton of the mixture (according to the size of the furnace) is shovelled in upon the preparatory bed, spread evenly over the surface, and transferred, when it has become hot, to the fluxing bed, which by this time should be at a full red heat. The mixture is transferred with the assistance of an iron tool, shaped somewhat like an oar. Whenever the first charge is shifted down upon the fluxing bed, a second charge should immediately be placed upon the preparatory bed.

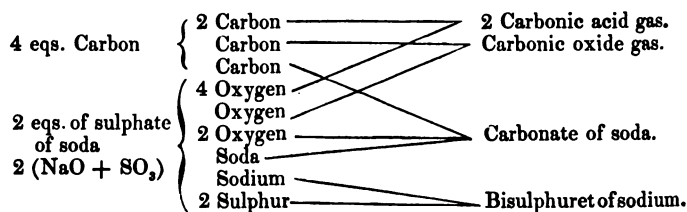
As soon as the mass on the fluxing bed becomes ignited, and begins to clot upon the surface, it is completely turned over by the oar or "spreader;" and in the course of a few minutes afterwards, when jets of inflamed sulphuretted hydrogen and carbonic oxide gases, called "candles," begin to issue from various parts of the mass, the whole must be expertly worked about with the "spreader" and an iron rake, in order to equalize the mass, and constantly expose fresh surfaces to the action of the flame. When the temperature of the mixture seems to fall below the proper decomposing heat, the stirring and spreading may be discontinued for a few minutes, and the door closed to allow the mass again to attain a state of bright ignition. The agitation is then recommenced with

vigour, and continued until the jets of flame nearly disappear, when the mass is raked out into cast-iron troughs, each capable of holding about three hundredweight. The time required for this part of the process of course varies with the quantity of material operated on; three hundredweight might easily be worked off in one hour, and a ton in about six hours, from the time the charge was first introduced. As soon as the first charge is raked out, the second is shifted from the preparatory bed to the fluxing bed, and a third charge immediately laid upon the preparatory bed. The product of this operation, which is known as black-ash, ball soda, and British barilla, should contain from twenty to twenty-four per cent. of available alkali; a ball of three hundredweight affords, on the average, one hundredweight and a quarter of soda-ash. The composition of black-ash varies considerably with the skill of the soda-furnacer: the principal insoluble constituents are, carbonaceous matters, carbonate of lime, and a compound of lime and sulphuret of calcium; the soluble ingredients are, carbonate of soda, undecomposed sulphate of soda and common salt, caustic soda, and generally some sulphuret or bisulphuret of sodium.

The operation which has just been described is the most important part of the soda process. By the fusion of sulphate of soda with coal, the former parts with either the whole or a portion of its oxygen, and is thereby reduced either to the state of sulphuret of sodium only, or else to a mixture of sulphuret of sodium and carbonate of soda. In effecting this abstraction of oxygen, the hydrogen of the coal plays

as important and active a part as the carbon; but in the following diagram, illustrative of this decomposition, the carbon of the coal may be supposed for the sake of simplicity to be the only reducing agent concerned.

REDUCTION OF SULPHATE OF SODA BY CARBON.



Such is the manner in which the decomposition of an alkaline sulphate by carbon is viewed by Professor Liebig. If carbon is present in a greater proportion, it is taken up by the carbonic acid gas, which thereby passes into the state of carbonic oxide.

By the fusion of sulphate of soda with carbonate of lime, as well as with coal, the sulphuret of sodium produced through the latter is converted into carbonate of soda. The calcium of the carbonate of lime and the sodium of the sulphuret exchange places, and the resulting substances are sulphuret of calcium and carbonate of soda. The calcination of sulphate of soda with both coal and carbonate of lime at the same time is by no means essential to the process: if desirable, the sulphate might first be heated with coal alone, and the resulting sulphuret, or mixture of sulphuret and carbonate, be afterwards calcined with carbonate of lime.

The success of the soda process is owing, in no small degree, to the apparently trifling circumstance, that sulphuret of calcium, which is soluble in water to a certain extent when unmixed with free lime, possesses the power of uniting with caustic lime to form a compound insoluble in cold water. When the soluble sulphuret of calcium is added to a solution of carbonate of soda, carbonate of lime is precipitated, and sulphuret of sodium remains in solution. If the sulphuret of calcium in black-ash were soluble in water, the carbonate of soda would therefore return to the state of sulphuret of sodium, on lixiviating the black-ash in water. But fortunately, the whole of the sulphuret of calcium in the black-ash is, or ought to be, in combination with lime as an insoluble compound, known in alkali works by the name of "soda-waste." The presence of an excess of lime is therefore essential to the success of the process. Though the sulphuret of calcium is not dissolved out from the soda-waste by cold water, yet very hot water effects the decomposition of the compound of sulphuret of calcium and lime, and consequently the solution of the sulphuret of calcium. Hence the application of very hot water to black-ash should be avoided.

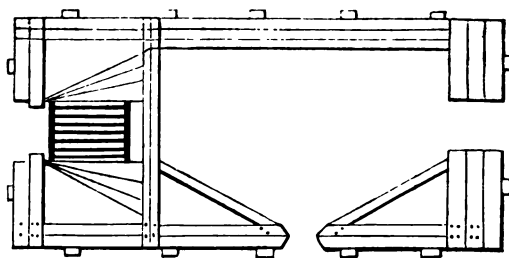
The next part of the process has for its object the separation of the soluble constituents of black-ash from the carbonaceous and other insoluble matters present. This is the first step towards the preparation of pure soda from black-ash.

For this purpose the balls of black-ash are broken into fragments, put into iron vats, and covered with water. In the course of ten or twelve hours, the

solution thus obtained may be drawn off through a hole near the bottom of the vat, and the residue in the vat may be washed six or eight times successively, either with fresh water, or else with the washings of other vats almost exhausted.

The solutions thus obtained being mixed are generally evaporated and the residue calcined in the same reverberatory furnace, generally called the "white-ash furnace," a horizontal section or ground-plan of which is shewn at fig. 46. The extreme length

Fig. 46.



of this furnace is about eighteen feet, and the breadth nine feet. Its interior is lined with fire-brick, between which and the external masonry is placed a partition of sheet-iron. By the application of heat in this manner, in the form of hot air from a fire, the evaporation proceeds rapidly, quietly, and at a very moderate expense of fuel. Instead of evaporating the liquid to dryness, and immediately calcining the residue, the contents of the furnace, when they have attained the consistence of mortar, are sometimes raked out into a large iron vessel furnished with a false perforated bottom, to allow the mother-liquor to drain from the crystals. This mother-liquor is of a dark

red colour, and contains in solution a considerable quantity of iron, probably as sulphuret in the form of a soluble combination with sulphuret of sodium. The drained mass is next collected, and introduced into a reverberatory furnace called the "finishing furnace;" in which it is moderately calcined, and at the same time dexterously worked about in all directions, so as to bring every part of it within the action of the flame and in contact with the air.

The residue of this operation, when ground under edge stones, is the "white-ash" or "soda-ash" of commerce: when the process has been properly managed, it contains very little of either caustic soda, sulphuret of sodium, or hyposulphite of soda. The article thus prepared is sufficiently pure for nearly all the ordinary manufacturing applications of soda; but for a few purposes, particularly for the plate-glass manufacture, and for making the crystallized carbonate, the ash made as above requires to be rendered still purer, and this is now commonly effected by giving it another calcination in a reverberatory furnace moderately heated, sometimes, by a charcoal fire. The objects of this calcination are to cause the expulsion of sulphur from the soda-ash, and the combination of all the particles of caustic soda in the ash with carbonic acid derived from the fire. The heat applied in this part of the process should not much exceed the melting point of lead. At that temperature the sulphur goes off freely; but at a dull red heat, the sulphur, instead of being volatilized, seems to enter into more permanent combination with the alkali. The alkali requires to be worked about with the oar and rake during the whole course of

this operation, which usually takes about three or four hours. The product is an excellent article for the plate-glass manufacturer. It is not usual at the present time to mix the carbonate with coal, saw-dust, or charcoal, in this part of the process, as was formerly practised.

To obtain the crystallized carbonate of soda, the purified ash is merely dissolved in hot water to saturation, and the solution is run into shallow crystallizing pans of cast iron or of wood lined with sheet-lead, and allowed to become cold. If the ash has been calcined with saw-dust, coal, or charcoal, it is lixiviated with water, the solution is allowed to settle, and the clear liquor is drawn off and evaporated until a pellicle forms upon its surface, when it is run into the crystallizing pans. The crystallization may be considered complete in a week or less ; the mother-liquor, which contains nearly the whole of the foreign salts, is then withdrawn and evaporated to dryness ; the residue generally contains about thirty per cent. of alkali, and serves for the crown-glass and soap manufactures.

A patent was obtained in 1841 by Mr. James Shanks, of St. Helen's, Lancashire, for processes for impregnating black-ash and white-ash with carbonic acid gas, for the purpose of converting the caustic soda and silicate of soda contained therein, into carbonate. In one of these processes the black-ash is broken into fragments and disposed in several layers each of three or four inches in depth, in a stone or iron vessel called the "carbonator." The layers having been moistened with water, carbonic acid gas is admitted into the

carbonator by a pipe, the air being allowed to escape by another pipe. When the odour of sulphuretted hydrogen is strongly perceptible at the exit pipe, the whole of the soda is considered to be carbonated; the introduction of carbonic acid is then discontinued, and the black-ash is removed to the vats, and lixivated in the ordinary manner. The ley prepared from black-ash may be exposed to the action of carbonic acid, instead of the solid ash itself. The carbonator used for this purpose should have a capacity of sixteen cubic feet for every ton of white-ash, or six cubic feet for every ton of soda-crystals, to be made daily. Across the bottom of the carbonator is thrown an arch of open brick-work, and the space above is filled with small pebbles, over which flows the solution to be carbonated, which is admitted at the top. The carbonic acid gas is introduced below the arch, and allowed to rise in the carbonator between the pebbles, the air of the vessel escaping by a pipe at the top. The liquor loses its greenish-yellow colour (which seems to be due to traces of sulphuret of iron held in solution by sulphuret of sodium) when sufficiently carbonated. In another process, the last or weakest soda liquor from the lixiviating vats is supersaturated with carbonic acid gas in the carbonator, and then used for lixiviating fresh charges of black-ash. Mr. John Wilson obtained in 1840 a patent for some improvements in the manufacture of carbonate of soda, which included the application of as much bicarbonate of soda to black-ash, or white-ash, as might be necessary to convert the whole of the caustic soda in the ash into carbonate.*

* Mr. Wilson's patent also included a mode of preparing carbonate of soda from sulphuret of sodium, by mixing with a solution of forty-eight

Besides the modifications of the common soda process which have been already described, several more considerable changes have been proposed, neither of which, however, has yet come into successful competition with the process of Leblanc.

A method of procuring caustic soda directly from common salt was long ago contrived by Mr. Turner, which consisted in intimately mixing and rubbing together one part of salt, from four to six parts of litharge (protoxide of lead), and a little water. Double decomposition takes place between the salt and a portion of the oxide of lead, with formation of caustic soda and chloride of lead: the former is dissolved out by water, and the latter remains in an insoluble state in combination with another portion of litharge as an oxi-chloride of lead. After being fused and levigated, the oxi-chloride forms the pigment known as "patent yellow." This mode of procuring soda has been abandoned as a manufacturing process, in consequence of the limited sale of the pigment.

To procure caustic soda directly from sulphate of soda, it has been proposed to decompose the sulphate by a solution of caustic barytes. When a solution of sulphate of soda is mixed with a solution of caustic barytes, the sulphuric acid of the sulphate unites with the barytes to form the insoluble sulphate of that earth; and if the mixture is made in the proper

parts of the sulphuret, eighty-five parts of bicarbonate of soda. If the sulphuretted hydrogen gas thus disengaged is to be collected, the materials may be mixed in a covered iron pan furnished with a pipe to conduct the gas to a gas-holder; but if the gas is not required, the operation may be carried on in a common white-ash furnace. The mixture is evaporated to dryness, the residuary carbonate is dissolved in water, and the clear solution is decanted and concentrated by evaporation.

proportion, nothing should remain in the solution but caustic soda. If an excess of barytes has been applied, it is precipitated as carbonate on evaporating the solution with access of air; or it may be more conveniently removed by adding an additional quantity of sulphate of soda. The difficulty of procuring with facility the requisite quantity of caustic barytes, will probably always prevent any process of this kind from becoming general.

An interesting process for obtaining carbonate of soda from common salt has been proposed by Messrs. Hemming and Dyer, which is founded on the comportment of a solution of salt with a solution of bicarbonate of ammonia. When the carbonate of ammonia of the shops, which contains bicarbonate of ammonia, is added in a state of fine powder to a solution of about an equal weight of salt in three parts of water, the mixture being well stirred, a white crystalline precipitate appears in a few hours, which causes the liquid to become thick. The precipitate is bicarbonate of soda, and the liquid contains in solution muriate of ammonia, these two substances being the products of the double decomposition of bicarbonate of ammonia and chloride of sodium.*

In the manufacturing process founded on this reaction it is proposed to commence by mixing with

* This decomposition is most simply stated on the ammonium theory, which supposes the muriate of ammonia and bicarbonate of ammonia to contain a radical composed of NH_4 , which is named ammonium, and which occupies in the ammoniacal salts the place of a metal, as potassium and sodium in the salts of potash and soda. Bicarbonate of ammonia may then be considered as a double carbonate of water and oxide of ammonium, or $\text{HO}, \text{CO}_2 + \text{NH}_4\text{O}, \text{CO}_2$, as bicarbonate of soda is the double carbonate of water and oxide of sodium; and muriate of am-

salt an impure carbonate of ammonia, such as the liquor furnished by the distillation of bones; and having separated the solid bicarbonate of soda by pressure in a screw-press, to reconvert the muriate of ammonia in the mother-liquor to carbonate, by evaporating the liquid to dryness, and heating the residue in a distillatory apparatus with carbonate of lime, as in the ordinary mode of preparing carbonate of ammonia. Unless particular precautions are adopted, the loss of ammonia in this process must be very great and inevitable, from two reasons: first, when a mixture of muriate of ammonia and carbonate of lime is heated, a portion of the ammonia is always disengaged in the free state, the product not being a neutral carbonate, but a sesquicarbonate, containing, to three equivalents of carbonic acid, two equivalents of ammonia. In this process, one eq. of ammonia out of three is disengaged in the free state as a gas, and lost, unless particular means are adopted to retain it. Again, when the sesquicarbonate of ammonia is dissolved in water, it is resolved into the neutral carbonate and the bicarbonate; but the common salt is decomposed by the bicarbonate only; the neutral carbonate remains in the mother-liquor, and is decomposed during the evaporation into free ammonia and the bicarbonate, both of which are volatilized. By making use of such an apparatus as would allow the ammoniacal gas and the bicarbonate of ammonia thus disengaged to be conducted into a condenser of some

ammonia as the chloride of ammonium, NH_4Cl ; or the analogue of chloride of sodium. On this view, the mutual decomposition of bicarbonate of ammonia and chloride of sodium is nothing more than the transposition of the ammonium in the former, and the sodium in the latter.

kind, this process might perhaps be found the most economical of all those for preparing carbonate of soda from salt.

The preceding process, with a slight modification, has been made the subject of a patent "for improvements in the manufacture of sal-ammoniac." The patentee proposes to impregnate the mixture of the two materials with as much carbonic acid gas as it will absorb, whereby the sesquicarbonate of ammonia is wholly converted into the bicarbonate. This is probably a decided improvement on the process of Messrs. Hemming and Dyer.

MM. Blanc and Bazille have proposed and patented a soda process founded on the decomposition of common salt by silica, at a high temperature and in the presence of steam. When the vapour of water is passed through an intimate mixture of common salt and siliceous sand, contained in a porcelain tube heated to bright redness, the salt is decomposed, its chlorine unites with the hydrogen of the steam to form hydrochloric acid which escapes as a gas, while its sodium unites with the oxygen of the steam and with the silica to form silicate of soda. This decomposition does not take place without the presence of water. The resulting silicate of soda may be freed from all undecomposed salt by lixiviation in water, in which the silicate is scarcely soluble. To procure the silicate in a state of solution, it is calcined with a little carbonate of soda in order to form a subsilicate which may be dissolved in water. From such a solution carbonate of soda may be obtained by impregnation with carbonic acid gas, which causes the precipitation of gelatinous silica. Carbonate of soda remains in solution.

In carrying out this process on a manufacturing scale, it is proposed to introduce the mixture of salt and siliceous sand into cast-iron cylinders arranged in furnaces in a manner similar to gas retorts, so that the flame may envelope them and raise them to a cherry-red heat. A large perforated tube for the introduction of steam, as long as the cylinder, is to traverse the axis of each cylinder; and from one extremity of the cylinder is to proceed a large porcelain or stone-ware tube for the purpose of conducting away the evolved muriatic acid. The latter tube should have a large orifice, to prevent its being choked up by volatilized salt; and it should lead into a large empty chamber in which the volatilized salt might be deposited. A communication should be established between this chamber and a series of stone cisterns containing a little water for the purpose of condensing the muriatic acid.

Each cylinder being loosely filled with an intimate mixture of twenty-eight parts of salt and twenty parts of sand, is to be raised to a cherry-red heat, and steam be slowly and steadily admitted into the perforated tube from a boiler. The mass thus obtained is to be lixiviated with water, to remove the undecomposed salt; and the washed silicate be calcined at a red heat with about six-tenths of its weight of carbonate of soda, until the mixture is vitrified. The resulting subsilicate may be employed in the glass manufacture; or else, to obtain carbonate of soda, it may be dissolved in water, and the solution be impregnated with carbonic acid gas, as before described. The patentees prefer procuring the carbonic acid gas from limestone by calcination in continuously acting

lime-kilns. To the top of the lime-kiln is adapted a dome-top, from which a tube passes into the vessel containing the solution to be carbonated. It is said that the draught through the kiln is quite sufficient to maintain a proper combustion to the end, if a large single vessel is employed to contain the solution, instead of several small vessels. It is probable that the manipulations required in these operations would be tedious, and the decomposition of the salt in the cylinders too slow and incomplete to allow of this process being carried on successfully on a large scale.

The principles on which is founded the patent for improvements in the manufacture of the fixed alkalies and their carbonates, obtained a few years ago by Mr. William Hunt, are briefly the following. When the product of the decomposition of sulphate of soda by coal or coke is lixiviated with water, and the solution (which contains sulphuret and bisulphuret of sodium, with caustic soda and carbonate of soda,) boiled with oxide of zinc or black oxide of copper, double decomposition ensues between the sulphuret of sodium and oxide of copper or oxide of zinc, with production of the insoluble sulphuret of copper or zinc and a solution of caustic soda. The metallic sulphuret obtained in this operation may be made available in the preparation of another quantity of sulphate of soda from common salt, with the reproduction of oxide of copper or oxide of zinc, by either of the two following methods: 1°, by burning it at a high temperature in a current of atmospheric air, and conducting the sulphurous acid thus produced into a leaden chamber to be converted into sulphuric acid in the ordinary manner; or, 2°, by roasting the

sulphuret at a temperature of about 400° F., with exposure to the air, whereby the metallic sulphuret is converted into sulphate. The sulphuric acid obtained by the first of these methods is applied to the salt in the usual manner, and the calcined oxide remaining as the residue of the sulphuret is again employed in the decomposition of sulphuret of sodium. The sulphate of copper or sulphate of zinc obtained by the second method, after having been freed from the accompanying oxide or unaltered sulphuret by lixiviation in water, may be mixed with a solution of common salt, whereby sulphate of soda and chloride of copper or chloride of zinc are produced. The alkaline sulphate may be separated from the metallic chloride by crystallization, and oxide of zinc or oxide of copper fit to be used for the decomposition of more alkaline sulphuret may be obtained from the mother-liquor by the addition of milk of lime. Or the metallic sulphate procured by roasting the sulphuret may be distilled at a bright red heat with a view of obtaining sulphuric acid, a small stream of air being allowed to pass through the distilling furnace, and the acid vapour and gases be conducted into a condenser similar to the sulphuric acid chamber.

§ IV. ALKALIMETRY.

The branch of chemical analysis termed alkali-metry has for its object the determination of the value of the carbonates of potash and soda met with in commerce, by making an estimation of the amount of available alkali they contain. The available alkali

is that which exists in the free or caustic state, and that which exists as carbonate. Two simple processes for obtaining this have been contrived, by which results of sufficient accuracy for all ordinary purposes may be obtained with ease, after a very little experience.

In one of these methods, the experiment consists in finding what quantity of an acid is required to destroy the alkaline reaction of a known weight of the specimen to be tested. The quantity of acid required for the neutralization of a soda-ash which contains none other than the usual impurities, common salt and sulphate of soda, is of course exactly equivalent to the quantity of soda present in the free state and as carbonate.

In this operation, a tube measure called an alkalimeter is employed (fig. 47), about fourteen inches in height, and five-eighths of an inch in diameter, mounted on a foot, and capable of holding, when quite full, a little more than 1,000 grains of water. It is graduated up to this amount into one hundred divisions, numbered from the top downwards; each division, therefore, represents ten grains of water.

Fig. 47.



The acid employed for the neutralization of the alkali is sulphuric, made of such a strength that a single measure of the alkalimeter (ten grains measure of water) is sufficient to neutralize exactly one grain of pure soda. Acid of this strength is obtained in the following manner: 170.6 grains of pure carbonate of soda (prepared by heating the bicarbonate to dull redness in a clean platinum or

porcelain crucible) are dissolved in four or five ounces of hot water. This quantity contains exactly 100 grains of pure soda. A quantity, say a pint, of a dilute acid is prepared by mixing one part of oil of vitriol with ten of water by measure, with which the alkalimeter is filled to 0 (1,000 grains measure of water), and poured from this very gradually into the solution of carbonate of soda above mentioned, until it has destroyed the alkaline reaction of the latter on test paper, and the mixture has become very feebly acid. The quantity of acid which has been required to produce this effect is accurately observed. Supposing it to be 90 measures, that quantity is of course equivalent to 100 grains of soda; but an acid is wanted, of which 100 measures instead of 90 are required to neutralize the soda: to procure this, we have simply to add to 90 volumes of the acid 10 volumes of water, so that the amount of real acid which was before contained in 90 shall now be contained in 100 parts. For this purpose, any vessel of sufficient capacity accurately divided into 100 equal parts will suffice. Such is the method of preparing the *test-acid*, of which 1 alkalimeter measure (10 grains of water) is equivalent to 1 grain of pure soda: 22 measures should neutralize 100 grains of crystallized carbonate of soda, and $58\frac{1}{2}$ measures 100 grains of anhydrous carbonate of soda.

In performing an actual analysis, 100 grains of the soda-ash to be tested are weighed and dissolved in about three ounces of hot water; the solution is filtered if any carbonate of lime is present, and neutralized with the test acid poured from the alkalimeter. The number of measures required represents the amount of soda per

cent. in the specimen. If 50 grains of the soda-ash are operated on instead of 100, the number of measures must of course be doubled to obtain the percentage of soda. The test-paper employed in alkalimetry should be exceedingly delicate;* and a distinction must be made between the purplish-red tint which carbonic acid produces, and the distinct reddening produced by sulphuric acid, which should be the indication to guide the operator. The slight reddening which carbonic acid produces may be discharged by the application of a gentle heat.

If the only impurities contained in the soda-ash to be tested are chloride of sodium, sulphate of soda, and insoluble matters, the process just described may afford results of sufficient accuracy; but frequently other bodies are present which interfere with this process by neutralizing a portion of the test-acid, such as sulphuret of sodium, and sulphite and hyposulphite of soda, which are liable to occasion a considerable error by taking up the sulphuric acid. One method of avoiding this source of fallacy consists in mixing the solution of the ash with chlorate of potash, evaporating to dryness, and heating the residue to redness; the sulphuret, sulphite, and hyposulphite are thereby converted into the sulphate of soda, which does not interfere in the process. A more convenient

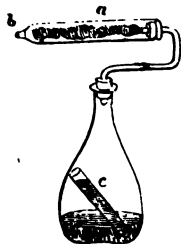
* The most convenient test-paper for alkalimetry is prepared by dipping good letter-paper several times into a concentrated infusion of the red cabbage. The infusion should be prepared by pouring hot water upon the cabbage in an earthenware (but not in a metallic) evaporating pan, and be concentrated by evaporation at a temperature considerably below the boiling point. The dull greyish paper thus made acquires a bright green colour by contact with alkalies, and a bright red colour by acids.

method of avoiding error from this source may be adopted when the soda-ash is tested by another alkalimetric process, to be noticed immediately.

The same test-acid used for soda may also be employed in the examination of the carbonates of potash; but as the equivalent of potash is higher than that of soda, the number of measures poured from the alkalimeter cannot represent the per-centage of this alkali, as it does that of soda. A simple calculation, however, reduces the numbers for soda to those for potash; their respective equivalents being very nearly as 4 to 6, the number of measures necessary to neutralize 100 grains of the specimen, multiplied by 6 and then divided by 4, gives the per-centage of potash required.

In the other alkalimetric process above alluded to, the proportion of real alkali is determined by observing the amount of carbonic acid gas disengaged on the neutralization of the carbonate, which amount is proportional to the quantity of pure alkali in the carbonate decomposed. But this process is of no value whatever when the soda-ash contains either caustic soda or bicarbonate of soda. The operation is conducted in the following manner: A known weight, say 50 grains, of the soda-ash to be tested, is introduced into a flask similar to

Fig. 48.



that represented in the annexed figure. The flask should be thin at the bottom to allow of the application of heat, and have the capacity of three or four ounces of water. It is fitted with a cork which has a perforation to admit a small bent tube, and the latter is connected by means of another cork with a somewhat larger tube *a*, containing

fragments of dry chloride of calcium. The extremity, *b*, of this tube is drawn out so as to be capillary. The small tube *c*, within the flask, is intended to hold sulphuric acid to decompose the carbonate, and is of such length that it will not fall flat on the bottom of the flask, but rest against the side at an angle of about 45° with the bottom, so that on inclining the flask, all the acid contained in this tube can be made to flow out. The apparatus being ready, the weighed carbonate is introduced into the empty flask, with about half an ounce of water; the small tube *c*, containing sufficient strong sulphuric acid to decompose the carbonate, is then introduced, care being taken that no acid comes into contact with the carbonate, and the flask is closed by the cork attached to the chloride of calcium tube. In this state the apparatus is carefully weighed. After the weighing, the flask is inclined, in order that a little of the acid in the tube *c* may flow out and come into contact with the carbonate; and the acid is poured out by little and little, until the carbonate is entirely decomposed. An excess of sulphuric acid occasions no inconvenience whatever. As the evolved carbonic acid gas is dried in its passage through the chloride of calcium tube, nothing else than this gas escapes, and the loss in weight of the apparatus at the close of the experiment is the weight of the carbonic acid required. But as the flask is now full of carbonic acid gas, which is considerably heavier than air, it should not be weighed in its present state. To get rid of the remaining carbonic acid, the flask is gently heated, so as to fill it with aqueous vapour, and thus drive out the gas; the steam itself should not proceed further than the

chloride of calcium tube. On the condensation of the steam, air enters the flask, which, when cold, is in the same condition, as to weight, as it was when weighed before the decomposition of the carbonate, save only in the loss of carbonic acid.

The carbonic acid gas remaining in the flask at the close of the decomposition may be more easily removed by affixing to the cork of the flask another small tube open at both ends; one end may reach nearly to the bottom of the flask, and the other an inch or so from the cork, so as to be conveniently closed by the finger during the decomposition, in order to prevent the passage of the gas through that tube. At the close of the decomposition the flask is very gently heated, merely to expel the carbonic acid dissolved in the acid solution; another chloride of calcium tube is then attached by a cork to the end of the open tube; and the carbonic acid having been first blown out through the tube *a*, by the mouth applied to the other chloride of calcium tube, fresh air is sucked in by applying the mouth to a perforated cork or small tube adapted to *b*. The flask is then in a fit state to be weighed.

If all the available alkali is in the state of neutral carbonate, and no sulphite or hyposulphite of soda or sulphuret of sodium is present to occasion an evolution of sulphurous acid or sulphuretted hydrogen, then the value of the soda-ash may be calculated from the loss in the weight of the flask at the close of the experiment: 22 parts (1 eq.) of the disengaged carbonic acid indicating 31·3 parts (1 eq.) of soda.*

* The following little table will serve to facilitate this calculation considerably:

1 part of carbonic acid indicates	1·4227 parts of soda.
2 parts	„ indicate 2·8454 „

The ingredients of soda-ash which would affect the results obtained by this process are carbonate of lime, sulphite and hyposulphite of soda, sulphuret of sodium, caustic soda, and bicarbonate of soda.

The inconvenience which arises from the presence of carbonate of lime, may be surmounted by dissolving the soda-ash in water and filtering the solution; but the filtered liquid requires to be concentrated by evaporation to a very small bulk, proportional to the size of the flask. This operation, however, rarely needs to be practised in testing soda-ash for commercial purposes.

The presence of sulphite or hyposulphite of soda or sulphuret of sodium may be detected by adding some of the soda-ash to dilute sulphuric acid, coloured reddish-yellow with bichromate of potash, the alkali not being added in sufficient quantity to saturate the acid. If the above salts are present, the reddish-yellow colour is changed to green, owing to the deoxidation of the chromic acid and formation of oxide of chromium. Soda-ash which contains sulphuret of sodium

3 parts of carbonic acid indicate 4.2681 parts of soda.				
4	"	"	5.6908	"
5	"	"	7.1135	"
6	"	"	8.5362	"
7	"	"	9.9589	"
8	"	"	11.3816	"
9	"	"	12.8043	"

As an example of the manner of using this table, suppose the amount of carbonic acid disengaged from 50 grains of soda-ash to be 17.7 grains; that is, 10.0, 7.0, and 0.7. The amount of soda indicated by 10 grains of carbonic acid is found by shifting the decimal point of the number for 1.0 to one figure to the right, which gives 14.227, the amount indicated by 7.0 grains is 9.9589, and that by 0.7 grains is 0.99589. The sum of these three numbers may be taken as 25.2, which multiplied by 2 gives the per-centage of alkali required.

gives a black precipitate with a solution of acetate of lead, and disengages the odour of hydrosulphate of ammonia when moistened with a solution of common carbonate of ammonia. To avoid the evolution of sulphurous acid or sulphuretted hydrogen during the operation, MM. Fresenius and Will recommend the addition to the soda-ash of a small quantity of yellow chromate of potash, the chromic acid of which serves to oxidize the sulphurous acid into sulphuric, and the hydrogen of the sulphuretted hydrogen into water, with separation of sulphur. As soda-ash is seldom or never altogether free from one of these impurities, the yellow chromate may be always added in this mode of testing, and the trouble of first ascertaining the presence of the sulphite, &c., by a preliminary experiment, be avoided.

One method of determining on the presence or absence of caustic soda in the carbonate of commerce, by observing the colour of the precipitate produced by nitrate of silver, has already been alluded to (page 416): another method consists in adding an excess of perfectly neutral chloride of barium to the soda-ash, treating the mixture with hot water and filtering; if the filtered liquid produces an alkaline reaction on test-paper, the presence of caustic soda may be inferred. Sulphuret of sodium would interfere with either of these tests, but the sulphuret is never found unaccompanied by the caustic alkali. Before a specimen of soda-ash containing caustic soda can be tested for its alkali by this process, the caustic soda must be converted into neutral carbonate. To effect this, the weighed sample may be rubbed up with from one-fourth to one-third of its weight of powdered carbonate

of ammonia, and three or four parts of siliceous sand; the mixture is placed in a porcelain capsule, thoroughly wetted with water, and then heated until the whole of the water and carbonate of ammonia is expelled (MM. Fresenius and Will). In this operation the caustic soda unites with the carbonic acid of the ammoniacal salt, and free ammonia is disengaged. When the odour of ammonia is no longer perceived, the mass is transferred to the flask and decomposed in the ordinary manner. The principal use of the sand is to prevent the mass from caking. When the soda-ash contains sulphuret of sodium, the carbonate of ammonia should first be mixed with sufficient solution of ammonia to convert the bicarbonate always present in the common carbonate into the neutral carbonate; the latter is without action on the alkaline sulphuret, but the bicarbonate of ammonia and sulphuret of sodium suffer mutual decomposition when placed in contact, water being also present. If the object of the experiment is to determine the relative proportions of caustic and carbonated alkali, the soda-ash may be operated on both before and after treatment with carbonate of ammonia, and the amounts of caustic and carbonated alkali be calculated from the difference in the results of the two experiments. The same object may also be attained by testing the soda-ash by both of the alkalimetric processes here described; by the first, to determine the entire proportion of alkali, and by the second, to determine the proportion of carbonic acid.

After lengthened exposure to the air, soda-ash sometimes contains a little bicarbonate or sesquicarbonate of soda, which would interfere with the re-

sults obtained by this method of alkalimetry, if present in an appreciable quantity. To detect the presence of the bicarbonate, the soda-ash is dissolved in water, mixed with an excess of solution of chloride of calcium, and the solution is filtered from the precipitate of carbonate of lime: the filtered liquid is then tested with pure solution of ammonia: if a precipitate or turbidity appears, the bicarbonate is present. The weighed sample of soda-ash must then be heated to dull redness to reduce the bicarbonate to neutral carbonate, before it can be tested by this process.

INDEX.

A.

Acid, test, for alkalimetry, 449.
 Alkalimeter, 449.
 Alkalimetry, 448.
 Alkaline leys for soap-making, 299.
 Alumina, silicate of, 15.
 Amidin, 104.
 Ammonia, use of carbonate of, as a
 "bate" in tanning, 205.
 Annealing of glass, necessity for, 21,
 22.
 Annealing-arch, 43, 54.
 Arrow-root, 139.
 " Brazilian, 140.
 " East Indian, 140.
 Arsenious acid, use of, in glass-making,
 32.

B.

Ball soda, 435.
 Barilla, 419.
 Barley, malting of, 153.
 "Bate," use of, in tanning, 204.
 Baurach, 261, *note*.
 Beaming or scraping of hides and skins,
 196.
 Bicarbonate of soda, 417.
 Bittern, 424.
 Black-ash, 435.
 "Black-ash furnace," 433.
 Bleaching of palm-oil, processes for,
 312.
 "Bloom," nature of, 215.
 Bologna phial, 20.
 British barilla, 435.
 Boracic acid, composition of the crude,
 282.
 " " how obtained from the
 lagoons, 274.
 " " native, 271, 279.
 " " origin of the, found in the
 lagoons, 279, 280, 281.
 " " preparation of borax from,
 283, 288, 289.

Boracic acid, properties and prepara-
 tion of, 267.
 Boracic lagoons, 271.
 Borates of soda, 290.
 Borax, 261.
 " history of, 261, *note*.
 " manufacture of, from boracic
 acid, 283, 288, 289.
 " mode of detecting sophistica-
 tion in, 289.
 " native, 261.
 " preparation of pure, from tincal,
 262.
 " present source of, 271.
 " properties and composition of,
 263.
 " use of, in blow-pipe analysis,
 265.
 " use of, in glass-making, 266.
 " use of, in making a glaze for
 earthenware, 266.
 " use of, in soldering, 266.
 Boron, 269.
 Bottle-glass, 60.
 Bottoming hole, 52.
 Brazilian arrow-root, 140.
 Brewing, principles of, 156.
 British sheet-glass, 55.
 Broad-glass, 55.
 Bromide of starch, 109, *note*.

C.

Caoutchène, 256.
 Caoutchine, 255.
 Caoutchouc, 245.
 " composition of, 251.
 " how formed into a block
 and sheets, 257.
 " introduction of, into Eu-
 rope, 256.
 " juice, properties, and com-
 position of, 246.
 " method of depriving threads
 of, of their elasticity,
 249, *note*.

Caoutchouc, method of making slabs of sand or saw-dust and, 259.
 " origin and preparation of, 245.
 " products of the distillation of, 254.
 " properties of, 248.
 " solvents of, 251, 252, 256.
 " stoppers for bottles, 256.
 " tubes, 249, *note*.
 " use of, for making a substitute for leather, 253.
 " use of, for making cloth water-proof, 252.
 " use of, for making "marine glue," 254.
 " use of, in book-binding, 253.
 " use of solutions of, 251.

Caoutchoucine, 254.
 " use of, as a solvent for caoutchouc, 256.

Casting plate-glass, 67.
 Cassava, 142.
 Catechu, 179.
 Cipipa, 142.
 Chamber, sulphuric acid, 374.
 Chamois leather, 239.
 Chloride of sodium, 423.
 Chromatic aberration, how prevented, 80.
 Colcar, 47.
 Colophonic acid, 320.
 Colouring of glass, 80.
 Copperas, 431.
 Cork-tree bark, 183.
 Crown-glass, 19, 46.
 " annealing of, 54.
 " materials for making, 48.
 " house, 46.
 Crystal, 35.
 " Cullet," 30.
 Curryng, 232.

D.

"Decomposing furnace," 426.
 Dextrin, 150.
 Diastase, 150, 152.
 Divi, 175.
 Drying oils, 208.

E.

East Indian arrow root, 140.
 Ellagic acid, 216.
 Etching on glass, 90.

F.

Ficus elastica, 245, *note*.
 Flashing furnace, 53.
 Flashing process, 51.
 Flint-glass, 19, 35.
 " density of, 10.
 " house, 35.
 " materials for making, 37.
 " modes of making vessels of, 40.
 " process of making, 38.
 Flour, composition of wheaten, 110, *note*.
 "Fluxing furnace," 433.
 Fritting of materials for making crown-glass, 49.

G.

Gallic acid, 169.
 German plate-glass, 55.
Glain acide of the Druids, 7.
 Glass, 1.
 " classification of different kinds of, 19.
 " colouring of, 80.
 " cutting and grinding of, 93.
 " defects in, 75.
 " devitrified, 22.
 " etching on, 90.
 " history of, 2.
 " how to obtain, of uniform density, 77.
 " invention of process of casting, 6.
 " knots in, 75.
 " manufacture of plate-, 62, 66.
 (See Plate-glass.)
 " malleable, 10, *note*.
 " materials for making, 24.
 " materials for making bottle-, 60.
 " materials for making crown-, 48.
 " materials for making flint-, 37.
 " mode of fashioning window-, 51.
 " mode of applying incrustations to, 90.
 " mode of making broad-, 55.
 " mode of annealing, 43.
 " modes of making vessels of, 40.
 " process of making crown-, 48.
 " process of making flint-, 38.
 " progress of manufacture of, in England, 7.
 " properties of, 9.
 " properties of unannealed, 21.
 " printing colours on, 88.
 " specific gravity of, 10.
 " striae in, 75.

- Glass, threads and tears in, 75.
 " use of arsenious acid in making, 32.
 " use of borax in making, 266.
 " use of oxide of manganese in making, 30.
 Glass-gall, 39.
 Glass-houses, usual form of, 33, 36.
 Glass-pots or crucibles, 33, 37.
 Glaze for earthenware, 266.
 Glue, Jeffrey's marine, 254.
 Gluten, 97, 109.
 Glycerine, 306.
 "Grainer," use of, in tanning, 204.
 Grape-sugar, *see* Starch-sugar.
 "Green fecula," 135.
 Green vitriol, 431.
- H.
- Heveène, 256.
 Hides and skins, 191.
 " " process for preserving, 231.
 Hides, liming of, 194.
 " preparation of, for tanning, 193.
 " unhairing of, 194.
 Hilum of the starch granule, 105.
 Hydrochloric acid, 428.
- I.
- India rubber, *see* Caoutchouc.
 Inferior window-glass, 55.
 Indian corn starch, 144.
 Inulin, 157.
 Iodide of starch, 108.
 Iodine, preparation of, from kelp, 421, *note*.
 Iron pyrites, use of, as a source of sulphur, 341, 353.
 " " use of, in the manufacture of sulphuric acid, 381.
 Iron, silicate of, 16.
- K.
- Kelp, 419, 420.
 Kid-leather, 237.
 Kips, 191.
 " preparation of, for tanning, 204.
- L.
- Lagoons, boracic, mode of working the, 274.
 Larch-bark, 181.
 Lead, oxide of, for making flint-glass, 29.
 " silicate of, 16.
 Leather, *see* Tanning, Tannin, Tawing, Currying, &c.
 " chamois, 239.
 " characters of good, 227.
 " enamelled, 237.
 " fancy, 233.
 " made with alum, 237.
 " morocco, 234.
 " new mode of preparing (Bordier's patent), 229.
 " Russia, 242.
 " substitute for, from caoutchouc, 253.
 Leblanc, invention of soda process by, 422.
 Leer-pans, 43.
 Leys, alkaline, for soap-making, 299.
 Lichenin or lichen starch, 157.
 Lime for glass-making, 26.
 " silicate of, 15.
 Liming of hides for tanning, 194.
- M.
- Mackintosh water-proof cloth, 252.
 Malleable glass, 10, *note*.
 Malting, 153.
 Manganese, use of oxide of, in glass-making, 30.
 Margaric acid, 294, 305.
 Margarine, 294, 302.
 Marine glue, Jeffrey's, 254.
 Marver, 40.
 Mimosa bark, 183.
 Morocco leather, 234.
 " imitation, 236.
 Mottled soap, 327.
 " " colour of the veins of, due to iron, 328.
 Moussache, 142.
 Mucilaginous starch, 150.
 Muriate of soda, 423.
 Muriatic acid, 428.
 Myrobalams, 182.
- N.
- Nitre and nitrate of soda, use of, in the manufacture of sulphuric acid, 377.

O.

Oak-bark, 173.
 Oil, purification of, 307, *note*.
 Oils, chemical constitution of fixed, 294.
 " drying, 308.
 Oleate of soda, 296.
 Oleic acid, 294, 306.
 Oleine, 294, 305.

P.

Palmitin, 311.
 Palm-oil, how obtained, 310.
 " present consumption of, 311.
 " processes for bleaching, 312.
 " properties of, 310.
 "Patent yellow" paint, 442.
 Pinic acid, 320.
 Plate-glass, 62, 66.
 " annealing of, 69.
 " blowing of, 74.
 " casting of, 67.
 " density of, 10.
 " invention of, 6.
 " materials for making, 63.
 " silvering of, 72.
 " works at Ravenhead, 65.
 Pontil, 41.
 Porcelain, Reaumur's, 22.
 Potash for glass-making, 27.
 " silicate of, 13.
 Potatoe, composition of, 125, 127.
 Potatoe-starch, apparatus for preparing, 132.
 " preparation of, 124.
 " uses of, 137.
 Potatoes, estimation of quantity of starch in, 128.
 Procello, 42.
 Plate-glass, grinding, smoothing and polishing of, 71.
 Pyrites burners for making sulphuric acid, 382, 383, 384.
 Pyrites, use of iron, as a source of sulphur, 341, 353.
 " use of iron, in the manufacture of sulphuric acid, 381.

R.

"Raising" of hides by acids, 199.
 Rasp for potatoes, 133.
 Ravenhead plate-glass works, 64.
 Reaumur's porcelain, 22.
 Rice, composition of, 118.
 Rice-starch, 118.
 Roan, 237.

Rock-salt, 424.
 Rosin, preparation and composition of, 319.
 Russia leather, 242.

S.

Sago, 141.
 Salep or Saloup, 143.
 Sal-gem, 424.
 Salt, action of sulphuric acid on common, 428.
 Salt-cake, 431.
 Salt, common, 423.
 Sand for making glass, 25.
 Sandiver, 39.
 Saponification, theory of, 294, 296, 297.
 Shell-lac varnish, 267.
 Silica or silicic acid, 10, 25, 26.
 Silicates, 12, 18, 19.
 Silicate of alumina, 15.
 " of iron, 16.
 " of lead, 16.
 " of lime, 15.
 Silicates of potash and soda, 13.
 Silicated soap, 329.
 Skin of animals, composition of, 163.
 " structure of, 163.
 Skins, mode of splitting, 228, *note*.
 " preparation of, for tanning, 204.
 Skiver, 237.
 Soap, 293.
 " chemical constitution of, 293, 294.
 " comportment of, with common salt, 323, *note*.
 " consumption of, in Great Britain, 334.
 " duty, arguments in favour of the repeal of the, 336.
 " manufacture of white, *see* White soap.
 " manufacture of soft, 331.
 " mottled, 327.
 " silicated, 329.
 " transparent, 331.
 " white, *see* White soap.
 " yellow, 329.
 Soap-making, "coppers" used in, 321.
 " "frames" used in, 326.
 " materials employed in, 299.
 " oily matters employed in, 301.
 " preparation of leys for, 300.
 Soaps, division of, into hard and soft, 295.
 Soda, bicarbonate of, 417.

